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PUBLISHED MONTHLY BY
WILLIAMS & WILKINS COMPANY
BALTIMORE, MD., U. S. A.

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.

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Price per volume, net post paid { $5.00, United States, Mexico, Cuba
$5.25, Canada
$5.50, other countries

SOIL SCIENCE

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INOCULATED SULFUR AS A PLANT-FOOD SOLVENT[1]

J. G. LIPMAN, A. W. BLAIR, W. H. MARTIN AND C. S. BECKWITH

New Jersey Agricultural Experiment Stations

Received for publication December 1, 1920

Earlier communications by the senior author and his associates (1, 2, 3, 4, 5, 6, 7) contain a review of the literature, as well as original data on the subject of sulfur oxidation by microorganisms. In this paper there are recorded the results obtained with dry inoculated sulfur when the latter was applied alone or mixed with inert phosphatic or potassic materials.

The experiments discussed in this paper were carried on at New Brunswick, Whitesbog and Elmer, New Jersey. In the first of these, tests were made with uninoculated and inoculated sulfur as a possible means for increasing the availability to the crop of the phosphorus in ground phosphate rock, and of the potassium in greensand marl. In this case a portion of a field representing the soil type known as Sassafras loam was used. The field in question was neglected for many years prior to 1908. In the spring of that year it was plowed and levelled off by means of a road scraper. For a dozen years after this it was cropped with rye, oats and Canada field peas and soybeans. No fertilizer except acid phosphate, applied at the rate of 200 to 250 pounds per acre, was employed during that period.

In the spring of 1920 the field was laid out in $\frac{1}{100}$-acre plots and utilized for two series of tests. The plots of series 1 received a uniform application of acid phosphate at the rate of 600 pounds per acre and of dried blood at the same rate. The additional treatments, on the acre basis, consisted of the following:

Plots 1–4	2000 lbs. greensand marl
Plots 5–8	500 lbs. uninoculated sulfur
Plots 9–12	2000 lbs. greensand marl and 500 lbs. uninoculated sulfur
Plots 13–16	500 lbs. inoculated sulfur
Plots 17–20	2000 lbs. greensand marl and 500 lbs. inoculated sulfur

The barley sown uniformly on May 17, came up unevenly. As the season progressed it was evident that the stand was much better on some of the plots than it was on the others. At the same time weeds sprang up in all of the space unoccupied by barley. Plots 14 and 15 were marked, more than the

[1] Paper No. 13, of the Technical Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

others, by a thin stand of barley and a particularly luxuriant growth of weeds. Repeated observations made between June 1 and the end of July showed that the crop on plots 4, 8, 12, 16 and 20 was much better than it was on the corresponding plots that had received the same treatment. The differences were readily accounted for by the fact that the portion of the field on which these plots were located was of better quality than the remaining portion of the field. The observations also showed that the plots which had received applications of inoculated sulfur, or of inoculated sulfur mixed with greensand marl, had a better growth of both weeds and barley than the other plots. The plants on the former looked more vigorous and had a more intense green color.

The unusually favorable rainfall conditions stimulated the growth of the crop on all of the plots. They interfered later with the drying of the crop after it was harvested. For this reason there was a considerable shrinkage in the weight of the crop between the time of harvesting and that of taking the final weights about three weeks later. During this period the sheaves of barley and weeds were exposed to constant wetting by the heavy rainfall of August. The resulting shrinkage fell most heavily on the crops from the more heavy-yielding plots. Hence the final weights as recorded do not do full justice to the returns obtained from the plots that had received applications of inoculated sulfur, or of inoculated sulfur and greensand marl. The yields secured from the several plots, expressed as pounds of air-dry matter per acre, are shown in table 1.

TABLE 1

Crop yields per plot, treated with sulfur and marl

PLOTS	WEIGHT OF CROPS				AVERAGE YIELD PER ACRE
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*
1–4	26	16	24	24	2250
5–8	22	21	17	23	2100
9–12	21	21	17	19	1950
13–16	26	26	24	26	2550
17–20	25	25	22	26	2550

For the reasons already noted undue stress should not be laid on the air-dry weights recorded in table 1. Nevertheless the larger returns obtained from plots 13 to 16 and plots 17 to 20 are in accord with the superior appearance of the crops on these plots as it was noted during the growing season.

In another series of tests the $\frac{1}{100}$-acre plots were treated as follows, calculated on the acre basis:

Plots 1–4 600 lbs. ground phosphate rock
Plots 5–8 200 lbs. uninoculated sulfur
Plots 9–12 600 lbs. phosphate rock and 200 lbs. uninoculated sulfur
Plots 13–16 200 lbs. inoculated sulfur
Plots 17–20 600 lbs. phosphate rock and 200 lbs. inoculated sulfur

Each plot received in addition to the above treatment 200 pounds each of ammonium sulfate and muriate of potash per acre.

As in the case of the sulfur-marl series, there were four plots of each treatment. The crop was also the same, namely, bearded barley. The observations as to weather conditions, weeds, etc., apply to this series as they do to series 1. The results secured are shown in table 2.

TABLE 2

Crop yields per plot, treated with sulfur and phosphate rock

PLOTS	WEIGHT OF CROPS				AVERAGE YIELD PER ACRE
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*
1–4	26	26	42	30	3100
5–8	25	18	42	40	3125
9–12	19	27	48	37	3375
13–16	16	20	41	44	3025
17–20	35	25	47	49	3900

It will be observed that the combination of inoculated sulfur and ground phosphate rock gave decidedly better yields than any of the other treatments in this series. The weights as recorded bear out the observations made during the growing season, namely, that the inoculated sulfur and phosphate treatments produced darker-colored and more vigorous plants. The leaves of the barley plants on these plots were broader and larger and showed every sign of stimulated growth.

Without laying undue weight on the numerical results recorded in table 2, it may be concluded that the inoculated sulfur had apparently served the crop better than uninoculated sulfur when used together with ground phosphate rock. It would seem also that the combination of uninoculated sulfur and ground phosphate was superior to the ground phosphate rock when the latter was used alone.

The experiments at Whitesbog were carried out on a coarse sandy soil, poorly drained and acid in character. Plots 264 feet by 12 feet were laid out and corn was drilled in rows that were 4 feet apart. The treatment of the several plots on the acre-basis and the yields of green corn obtained are shown in table 3.

It appears from the results recorded in table 3 that the land used in this experiment was deficient in phosphorus, since the no-treatment plot as well as that receiving nitrogen, potash and sulfur, gave low yields. All of the treatments which included phosphorus gave marked increases in yield. The acid phosphate produced lower yields than did the rock phosphate used alone or in combination with sulfur. It also appears that the mixture of inoculated sulfur and rock phosphate (plot 6) gave better returns than the mixture of uninoculated sulfur and rock phosphate (plot 4). On the whole, the green weights as recorded are in agreement with the observations made during the

growing season. They seem to indicate that mixtures of inoculated sulfur and rock phosphate may supply economically and effectively both the phosphorus and sulfur requirements of crops.

Loam of very good quality was used for the experiments at Elmer. The land had been in grass until the midsummer of 1920. After plowing and fitting it was planted with Irish Cobbler potatoes, which were to be used ultimately for seed purposes. The land used in the experiment was rather uniform in

TABLE 3

Treatments and yields of corn in experiment at Whitesbog

PLOT NUMBER	TREATMENT PER ACRE	YIELD OF GREEN CORN PER ACRE
		lbs.
1	Nothing	9,657
2	75 lbs. nitrate of soda 75 lbs. dried blood 300 lbs. acid-phosphate 25 lbs. muriate of potash	14,202
3	75 lbs. nitrate of soda 75 lbs. dried blood 300 lbs. rock-phosphate 25 lbs. muriate of potash	18,450
4	75 lbs. nitrate of soda 75 lbs. dried blood 300 lbs. rock-phosphate 100 lbs. sulfur 25 lbs. muriate of potash	17,316
5	75 lbs. nitrate of soda 75 lbs. dried blood 100 lbs. sulfur 25 lbs. muriate of potash	10,710
6	75 lbs. nitrate of soda 75 lbs. dried blood 300 lbs. rock-phosphate 100 lbs. sulfur 25 lbs. muriate of potash and sulfofying bacteria	19,224

character, but the section represented by series 2 was of better quality than that of series 1. Each of the plots was equivalent to 1/45.2 acre in area. All of the plots except no. 1 and 7, which served as checks, received an application of nitrogen at the rate of 80 pounds per acre, and of potash at the rate of 100 pounds per acre. One-half of the nitrogen was derived from nitrate of soda and the other half from sulfate of ammonia. The potash was derived from muriate. The additional treatments consisted of 200 pounds per acre of

sulfur on plot 3. It will be observed therefore, that plots 2 and 3 received an application equivalent to that of a 4-0-5 fertilizer at the rate of 2000 pounds per acre; while plots 4, 5 and 6 received an application of the same fertilizer and in addition, equal weights of phosphatic material. There was, however, a difference in the amount and source of phosphorus used on plots 4, 5, and 6. For the first of these the phosphorus was supplied in 1000 pounds of acid-phosphate, for the second in 1000 pounds of rock-phosphate, while for plot 6 it was supplied in a mixture of 200 pounds of inoculated sulfur and 800 pounds of rock-phosphate. Hence the acid-phosphate supplied 160 pounds of total phosphoric acid. The corresponding amount for the rock-phosphate was 320 pounds; and for the bacsul-phosphate 256 pounds. The potatoes were planted

TABLE 4

Yield of potatoes on plots variously treated at Elmer

PLOT NUMBER	TREATMENT PER ACRE	YIELD PER ACRE			CALCULATED YIELD OF CHECKS	INCREASE PER ACRE OVER CHECKS
		Series 1	Series 2	Average		
		bushels	*bushels*	*bushels*	*bushels*	*bushels*
1	Check	101.8	113.8	107.8		
2	80 lbs. N, and 100 lbs. K_2O	115.2	122.4	118.8	105.2	13.6
3	80 lbs. N, 100 lbs. K_2O, and 200 lbs. sulfur	91.1	124.3	107.7	102.7	5.0
4	80 lbs. N, 100 lbs. K_2O, and 160 lbs. P_2O_5 (acid-phosphate)	151.9	182.3	167.1	100.2	66.9
5	80 lbs. N, 100 lbs. K_2O, and 320 lbs. P_2O_5 (rock-phosphate)	107.7	126.4	117.0	97.7	19.3
6	80 lbs. N, 100 lbs. K_2O, and 256 lbs. P_2O_5 (bacsul-phosphate)	111.4	158.5	134.9	95.2	39.7
7	Check	87.4	98.0	92.7		

on August 5 and harvested November 5. The growing period corresponded, therefore, to the months of August, September and October, a time when the soil temperatures were gradually becoming lower and the conditions less favorable for the biological oxidation of the sulfur. The yields, expressed in terms of bushels per acre, are recorded in table 4.

It will be noted in the first place, that the soil responded to phosphorus treatment. The addition of phosphatic material increased in all cases the yield of the potato crop. Where acid-phosphate was used the increase was at the rate of 66.9 bushels per acre. Where rock-phosphate was used the increase was at the rate of 19.3 bushels per acre. Where bacsul-phosphate (the commercial name for mixtures of inoculated sulfur and ground phosphate-rock)

was used, the increase was at the rate of 39.7 bushels per acre. It would seem, therefore, that notwithstanding the well known preference of the potato crop for readily soluble phosphates, as well as the decreasingly favorable temperatures for the oxidation of the sulfur, the returns from bacsul-phosphate were far from unsatisfactory. At any rate, the data given in table 4 would justify the assumption that under suitable conditions bacsul-phosphate may prove to be an acceptable as well as an economical source of phosphorus for growing crops.

CONCLUSIONS

1. Inoculated sulfur seems to be more effective than uninoculated sulfur for rendering inert mineral plant-food accessible to growing crops.

2. Mixtures of inoculated sulfur and ground phosphate rock gave better returns than phosphate rock alone. Such mixtures may, after further experimentation, prove to be a satisfactory and economical source of available phosphorus.

REFERENCES

(1) LIPMAN, J. G., AND JOFFE, J. S. 1920 The influence of initial reaction on the oxidation of sulfur and the formation of available phosphates. *In* Soil Sci., v. 10, no. 4, p. 327–332.

(2) LIPMAN, J. G., AND MCLEAN, HARRY C. 1917 Vegetation experiments on the availability of treated phosphates. *In* Soil Sci., v. 4, no. 4, p. 337–343.

(3) LIPMAN, J. G., AND MCLEAN, H. C. 1918 Experiments with sulfur-phosphate composts conducted under field conditions. *In* Soil Sci., v. 5, no. 3, p. 243–250.

(4) LIPMAN, JACOB G., MCLEAN, HARRY C., AND LINT, H. CLAY 1916 The oxidation of sulfur in soils as a means of increasing the availability of mineral phosphates. *In* Soil Sci., v. 1, no. 6, p. 533–539.

(5) LIPMAN, JACOB G., MCLEAN, HARRY C., AND LINT, H. CLAY 1916 Sulfur oxidation in soils and its effect on the availability of mineral phosphates. *In* Soil Sci., v. 2, no. 6, p. 499–538.

(6) MARTIN, WILLIAM H. 1920 The relation of sulfur to soil acidity and to the control of potato scab. *In* Soil Sci., v. 9, no. 6, p. 393–408.

(7) MCLEAN, HARRY C. 1918 The oxidation of sulfur by microorganisms in its relation to the availability of phosphates. *In* Soil Sci., v. 5, no. 4, p. 251–290.

THE INFLUENCE OF IRON IN THE FORMS OF FERRIC PHOSPHATE AND FERROUS SULFATE UPON THE GROWTH OF WHEAT IN A NUTRIENT SOLUTION[1]

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New Jersey Agricultural Experiment Station

Received for publication November 25, 1920

The use of iron in nutrient solutions for plants has not received the attention which the importance of this element as a necessary requirement for growth and development deserves. Many investigations bearing upon the general problem of the salt requirements of plants have been carried out and the development of our knowledge concerning the relation of green plants to the mineral elements essential to their growth has come largely through the use of nutrient solutions in these investigations. Many opportunities for constructive research may still be found in the general problem of the salt requirements of plants, and nutrient solutions will surely have to be employed in experiments dealing with this problem since the mineral elements essential to plant growth can not be supplied to the plants except in the form of aqueous solutions.

No nutrient solution is complete without iron. Many of the formulas of standard nutrient solutions which have been proposed for use in culture studies specify neither the kind (molecular composition, soluble or insoluble) nor the quantities of iron to be employed. The opinion has been pretty generally accepted that a trace of iron, in whatever form it may be found most convenient to supply it to the plants in culture solutions, is sufficient for the needs of growing green plants. However, investigations of the conditions under which plants can best obtain the iron necessary for their growth and development and studies of the different compounds of iron and the proper concentrations of these which are best adapted for absorption and assimiliation by plants of different species under given sets of experimental conditions have been largely neglected within recent years.

The efficiency of the usual "trace" of iron when employed in culture solutions must certainly vary with the nature of the compound in which it is supplied to the plants, with the different species of plants, and with the nature of the solution in which it is employed. Corson and Bakke (1) have pointed out that the amount of iron used in nutrient solutions is probably of greater importance than is generally supposed. These authors have shown that ferrous

[1] Paper No. 11 of the Technical Series, New Jersey Agricultural Experiment Stations, Department of Plant Physiology.

iron is less efficient than ferric iron when used in the forms of phosphates, and that the difference in the efficiency of these two forms of iron supplied to the plants in a nutrient solution is not nearly so pronounced with Canada field peas as it is with wheat. However, the plants were grown during a period of only 24 days, and as Tottingham and Beck (4) have pointed out the amount of reserve iron in the seed is probably one of the most important factors determining the response of plants to the supplies of iron during the early stages of development. Gile (2) has shown that the condition of the nutrient solution (whether acid, neutral, or alkaline) has a very marked influence upon the availability of iron to rice plants.

On the following pages are reported the results of a brief study of the influence of varying amounts of iron upon the growth and general appearance of spring wheat when supplied to the plants in a nutrient solution in the forms of the insoluble ferric phosphate and the soluble ferrous sulfate, these two forms of iron being chosen as adding no new ions to the nutrient solution employed.

In this study spring wheat of the "Marquis" variety was used and the general culture method adopted by Shive (3) was followed throughout. The seeds were sprouted on a germinating net and when about 4 cm. tall three selected seedlings for each culture were mounted in cork stoppers of the proper size and were transferred to the culture vessels which consisted of quart fruit jars of colorless glass. Shive's three-salt solution number R_5C_2, having an osmotic concentration value of 1.75 atmospheres, was employed in all the cultures. Two series of ten cultures each were thus prepared. These will be designated series 1 and series 2 according as ferric phosphate and ferrous sulfate, respectively, were supplied as the source of iron. The culture solutions throughout each series differed only in the amounts of iron supplied while corresponding cultures of the two series differed only in the kind of iron used.

The ferric phosphate used in the culture solutions was prepared by precipitation from a dilute solution of ferric nitrate with a solution of mono-potassium phosphate. The precipitate was thoroughly washed, after which it was made into a suspension by the addition of distilled water and the iron was then determined by quantitative analysis of samples of the uniform suspension, and the total quantity adjusted, by the addition of distilled water, to contain 1 mgm. of iron in each cubic centimeter of this suspension which was used as a stock supply. Baker's "analyzed" ferrous sulfate crystals were used to supply iron in the soluble form. This form of soluble iron was chosen because it does not precipitate nearly so rapidly nor so completely from the culture solution here employed as do other forms of soluble iron such as ferric nitrate from which the iron is precipitated very rapidly and very completely as ferric phosphate. A stock solution of ferrous sulfate of such concentration that each cubic centimeter contained 1 mgm. of iron was freshly prepared each time just before being used in the culture solution. This was considered necessary since this salt in aqueous solution upon standing forms insoluble basic ferric sulfate as an oxidation product.

The cultures of series 1 contained iron in the phosphate form varying in amounts from 0.01 mgm. to 5.0 mgm. of iron per liter of solution, while the corresponding cultures of series 2 were supplied with the same amounts of iron in the form of ferrous sulfate. The solutions were renewed regularly at intervals of from $3\frac{1}{2}$ to 4 days during a growth period of 90 days, at the end of which time the plants were well past the flowering stage. It was the plan of the experiment to grow the plants to maturity but unfortunately an attack of mildew (*Erysiphe germinis*) made it necessary to discontinue the cultures considerably before the seed had matured.

In table 1 are presented the numerical data of the experiment including the amounts of iron as such supplied to each culture in milligrams per liter of

TABLE 1

Total dry weights of wheat plants grown 90 days in Shive's three-salt solution No. R_5C_2 supplied with varying amounts of iron in the form of ferric phosphate and ferrous sulfate

CULTURE NUMBER	IRON PER LITER OF SOLUTION	SERIES I, $FePO_4$		SERIES II, $FeSO_4$	
		Total dry weight (3 plants)	Number of heads per culture	Total dry weight	Number of heads per culture
	mgm.	*gm.*		*gm.*	
1	0.01	4.55	0	10.95	0
2	0.10	5.75	0	14.65	0
3	0.25	8.20	0	15.95	1
4	0.50	10.35	0	12.80	1
5	0.75	12.05	0	27.40	9
6	1.00	14.90	0	18.75	4
7	1.50	16.25	0	19.15	2
8	2.00	20.50*	0	23.50	2
9	3.00	18.00	0	20.90	3
10	5.00	16.85	1	18.45	4
Check	0.00	8.40	0		

* Two plants only, calculated for three.

nutrient solution, the total dry weights of tops and roots, and the number of heads produced by the plants of each culture.

During the fourth week of the growth period the plants of series 1, in the cultures having the lowest amounts of iron, began to show the yellowish color in the leaves which is characteristic of plants suffering from an insufficient supply of iron. This chlorotic and general unhealthy condition of the plants gradually spread as time went on until the plants of all the cultures were affected, although it was at no time markedly pronounced in the plants of the culture containing the highest amount of iron. There was a uniform decline in the severity of the chlorotic condition of the plants in passing from the culture containing the lowest to that containing the highest amount of iron. In this series only a single head was produced, this occurring in the culture having the highest amount of iron.

The condition of the cultures in series 2 presents a sharp contrast to that of the cultures in series 1. The plants of all the cultures in series 2, except those in cultures 1 and 2, appeared healthy and vigorous throughout the entire growth period, aside from the attack of mildew which occurred shortly before the time of harvesting. The plants in cultures 1 and 2 which contained very small amounts of iron were chlorotic and produced no heads. All the other

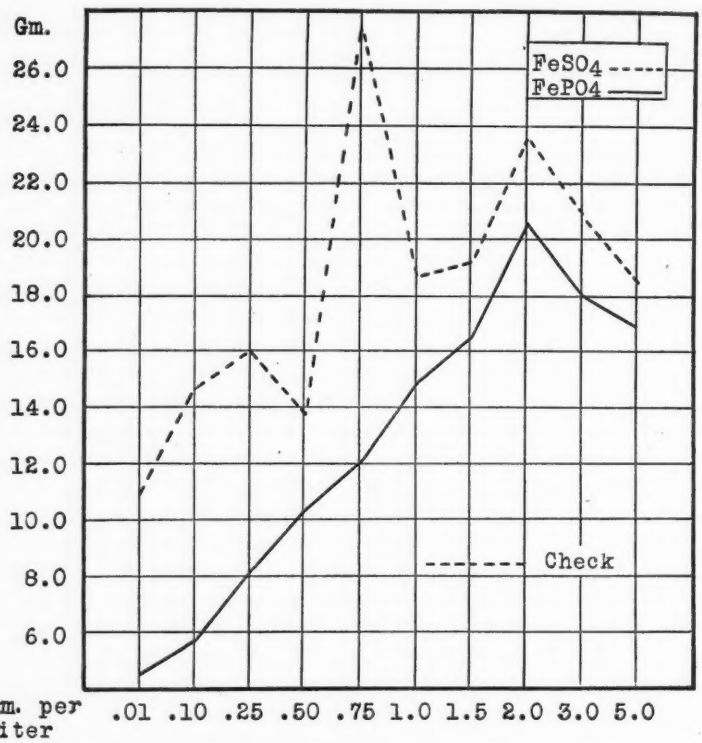

FIG. 1. TOTAL DRY WEIGHTS OF WHEAT PLANTS GROWN IN A NUTRIENT SOLUTION SUPPLIED WITH VARYING AMOUNTS OF IRON IN THE FORM OF FERRIC PHOSPHATE AND FERROUS SULFATE

cultures in this series produced heads the great majority of which were large and well formed. The general condition of cultures from each series about a week before the time of harvesting is shown photographically in plate I. These are corresponding cultures of the two series each supplied with the same amount of iron (0.75 mgm. per liter of solution), the one on the left receiving its iron in the form of ferrous sulfate, the one on the right in the form of ferric phosphate.

The total dry weight yields from the cultures of the two series as given in table 1, are shown graphically in figure 1. The dry weights as ordinates are here plotted against the amounts of iron in milligrams as abscissas. It will be observed that the yields from series 2 are much higher throughout than are those from series 1. The graphs of both series show a marked increase in yield with an increase in the amounts of iron supplied to the solutions up to an optimum which is not the same in both series. The maximum yield in series 1 was produced by the culture supplied with 2 mgm. of iron in the form of ferric phosphate while the maximum yield in series 2 was produced in the culture containing less than half this amount of iron in the form of ferrous sulfate. Both series show a marked decilne in yields from the cultures containing more than 2 mgm. of iron per liter of solution. In the cultures of series 2 this may be the result of a toxic influence of too high concentrations of the soluble ferrous sulfate, although the general appearance of the plants in these cultures did not indicate this. On the other hand, the plants in the corrresponding cultures of series 1, judging from the color of the leaves and the general appearance of the plants, suffered from an inadequate supply of iron, but the cause of the decline in yields is not clear. That the yellowish appearance of the leaves of the plants in the cultures of this series which were supplied with the highest amounts of iron was caused by the inability of the plants to secure the iron necessary for normal growth from the insoluble phosphate, was clearly demonstrated by the fact that duplicate cultures from this series when supplied with equivalent amounts of iron in the form of the soluble ferrous sulfate regained the normal green color of healthy plants in the course of two or three days.

It is thus clear that in the nutrient solution here employed iron in the form of ferric phosphate is very slowly and difficultly available to wheat plants even when supplied in relatively large quantities. Ferrous sulfate, on the other hand, appears to be readily available to these plants but is evidently somewhat toxic in the highest concentration used.

From the above considerations it appears that the insoluble ferric phosphate is not suitable for use with spring wheat in the culture solution here employed if the plants are to be grown beyond the stage of development when the reserve iron in the seed is no longer adequate to supply the needs of the plants. Ferrous sulfate, on the other hand, gave most excellent results when supplied to the culture solution here used in quantities of 0.75 to 3.0 mgm. of iron per liter of solution.

The limited experimental evidence here presented is only preliminary to a much more extended and complete study and does not justify the drawing of broad or definite conclusions, but the important generalizations touched upon will surely warrant more thorough investigation.

REFERENCES

(1) CORSON, G. E., AND BAKKE, A. L. 1917 The use of iron in nutrient solutions for plants. *In* Proc. Iowa Acad. Sci., v. 24, p. 477–482.

(2) GILE, P. L., AND CARRERO, J. O. 1920 Cause of lime-induced chlorosis and availability of iron in the soil. *In* Jour. Agr. Res., v. 20, p. 33–62.

(3) SHIVE, J. W. 1915 A study of physiological balance in nutrient media. *In* Physiol. Res., v. 1, p. 327–397.

(4) TOTTINGHAM, W. E., AND BECK, A. J. 1916 Antagonism between manganese and iron in the growth of wheat. *In* Plant World, v. 19, p. 359–370.

PLATE 1

EFFECT OF DIFFERENT FORMS OF IRON ON THE WHEAT PLANT

The culture on the left received 0.75 mgm. of iron per liter of solution in the form of ferrous sulfate; the culture on the right received an equivalent amount of iron in the form of ferric phosphate

NITROGEN IN THE RAINWATER AT ITHACA, NEW YORK

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Received for publication November 27, 1920

Since the middle of the Eighteenth Century it has been known that rainwater and snow contain nitrogen. The knowledge of this fact and the prime importance of nitrogen in agricultural practice have resulted in considerable work having been done to determine the amount of this element which the soil may receive from time to time through these agencies. As a rather full review of the literature on this subject is presented by Miller (7), in a report published in 1905 on the quantity of nitrogen and chlorine in the rainwater collected at Rothamsted, England, with one exception the writer will review only some of the articles which have appeared since that time.

Russell and Richards (8) have reported on the amount and composition of the rain falling at Rothamsted for a period of 28 years. It was found that, with an average annual rainfall of 28.82 inches, the ammoniacal nitrogen content was, on the average, 2.64 pounds per acre annually, while the nitric nitrogen was about one-half as much, or 1.33 pounds per acre. Monthly examinations of rainwater composed of daily collections showed the nitric nitrogen to vary only slightly from month to month, while the ammoniacal nitrogen was found to be highest during May, June, July and August and lowest during January, February, March and April. The yearly and monthly fluctuations in pounds per acre for both forms of nitrogen in the rainwater were generally in the same direction as were those for the rainfall, although this was not always the case. Since a close relationship was found between the amounts of ammoniacal and nitric nitrogen, the authors suggest a common origin or the conversion of ammoniacal forms into nitric forms. In addition to the ammoniacal and nitric nitrogen a yearly average of 1.35 pounds per acre of organic nitrogen was reported to be present in the rainwater. The sources of nitrogen are believed to be the sea, city pollution and the soil, the latter being an important source as the ammonia content of the rainwater is high and low at periods corresponding to high and low biochemical activity in the soil.

Crowther and Ruston (1) made analyses of rain collected for a period of 3 years at Garforth, England, and for a period of 12 months at different stations in the city of Leeds, England. An average annual rainfall of 26.95 inches at Garforth was found to contain 6.43 pounds of ammoniacal nitrogen and 1.93 pounds of nitric nitrogen to the acre. At Leeds the quantity of nitrogen in the rainwater varied at the different stations, ranging from 7.8 pounds per

acre to 18.4 pounds. In all cases the nitrogen was present largely in the form of ammonia or ammonium compounds, and it was only at stations some distance from the center of the city that nitrates could be detected at all. Organic nitrogen was found most abundant in the industrial area. The high nitrogen content of the rainwater collected at both Garforth and Leeds is attributed to the fact that they are situated in a large industrial center where the atmosphere is rich in impurities, notably ammonia.

With an annual rainfall of 32.55 inches at Flahult, Sweden (2) for the year 1909, von Feilitzen and Lugner found the rainwater to contain 3.32 pounds of ammoniacal nitrogen and 1.30 pounds of nitric nitrogen per acre. Their results show the nitrogen to vary considerably from month to month but the tendency is for both forms to be highest during the summer months.

Hudig (3) reports that an average yearly rainfall of 27.6 inches in the Province of Groningen, Netherlands, supplied an acre of soil with 4.54 pounds of ammoniacal nitrogen and 1.46 pounds of nitric nitrogen. It is stated that the amount of atmospheric nitrogen in the rainwater depends not only on the quantity of rain but on other meteorological conditions.

The monthly analyses of the rainwater collected for a period of 2 years at Bloemfontein and Durban in the Union of South Africa, reported by Juritz (4), show the summer rains to contain more nitrogen than the winter rains and the average amounts of nitrogen brought down yearly on the acre basis as ammonia and nitrates to be 4.02 pounds and 1.39 pounds, respectively.

Shipley (9) has reported the quantity of ammoniacal and nitrous nitrogen in the rainwater of Southwestern Alaska near Kashvik Bay during a rainy period in August, 1917. Ammonia was found to be almost entirely absent in the rainwater, which the author states is in striking contrast with the amount found at a similar latitude in Europe. Nitrous nitrogen was reported present in every sample of rainwater, with one exception, but the amount was always exceedingly small. No determinations were made for nitrate nitrogen.

Shutt and Dorrance (10) report the nitrogen compounds found in rainwater at Ottawa, Canada, for a period covering 10 years, during which time 897 samples were analyzed, 616 of which were rain and 281 of which were snow. Because of the greater solvent action of rain it was found to be much richer in nitrogen than was snow. With an average yearly precipitation of 23.39 inches for the decade, the soil received an annual supply of 6.58 pounds of nitrogen to the acre. Of this amount 3.41 pounds were in the form of free ammonia, 1.01 pounds in the form of albuminoid ammonia, and 2.16 pounds in the form of nitrates and nitrites. The writers point out that if the availability of this nitrogen is assumed to be equal to that in the more soluble nitrogenous fertilizers, the soil received during the 10 years reported an application of nitrogen equivalent to 440 pounds of sodium nitrate per acre. The rainwater contained its largest amount of nitrogen in August. This was true for all the forms of nitrogen studied except during September and October, 1908, when the free ammonia was unusually high on account of smoke contamination from

bush fires. Free ammonia gave the widest variation from month to month while albuminoid ammonia remained the most constant. Nitrate nitrogen was not found to be increased in the rainwater by electrical storms.

Several reports have been made on the nitrogen contained in rain and snow for short periods at Mt. Vernon, Iowa. For the period beginning January 12, 1910, and continuing for one year with the exception of the months of May, June, July and August, Knight (5) found in 17 samples of rain and snow, representing 6.81 inches of rainfall, nitrogen equivalent to 13.71 pounds per acre. Of this amount 2.04 pounds were in the form of free ammonia, 1.50 pounds in the form of albuminoid ammonia and 10.17 pounds in the form of nitrites and

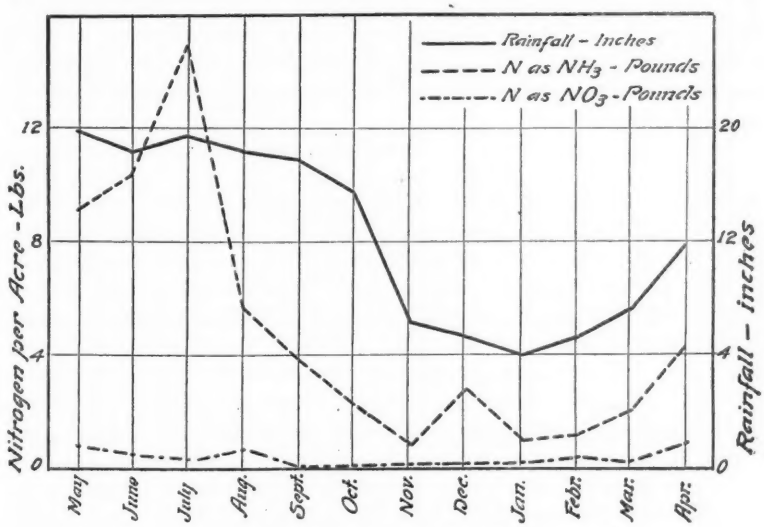

FIG. 1. RELATION OF NITROGEN TO RAINFALL
Period: May 1, 1915, to May 1, 1920

nitrates. These values for the different forms of nitrogen are quite different from those reported by Trieschmann (12) from the same place for the period between October 1, 1918 and June 15, 1919, when 46 samples of rain and snow representing a rainfall of 22.25 inches contained 5.28 pounds of nitrogen to the acre, 2.05 pounds being present in the rainwater as free ammonia, 1.84 pounds as albuminoid ammonia, 1.29 pounds as nitrate nitrogen and 0.09 pound as nitrite nitrogen. The latter author states that high winds and electrical discharges were not found to increase the quantity of nitrogen in the rainwater, that the total quantity of nitrogen found depends largely on the amount of rainfall, although an examination of the nitrogen supplied to the acre by each of the 46 precipitations showed a remarkable uniformity, and that rain was found to be richer in nitrogen than snow. While Knight found free ammonia

to be greater in rain than in snow he reports the latter, on the average, to contain more nitrites and nitrates.

The nitrate nitrogen found in the rainwater at Mt. Vernon for the first period mentioned above is exceedingly large and the relation of ammoniacal to nitrate nitrogen quite unusual. Miller (7) presents in tabular form the amounts of ammonia and nitric nitrogen found to be present in the rainwater of temperate and tropical countries. In the non-tropical rain where analyses were continued for at least four years, Lincoln, New Zealand, was the only one of ten different places where the nitric nitrogen was found to be in excess of the ammoniacal nitrogen. This relation was due to an unusually small amount of ammonia rather than to a high nitric nitrogen content. The rainwater of the tropical countries listed contained more nitrogen as ammonia than as nitric nitrogen, except that falling in British Guiana and Barbados. In neither place, however, was the yearly quantity of nitric nitrogen greater than 3.88 pounds to the acre.

As data on the nitrogen in the rain falling in this country are quite limited the report of Tracy (11) on the quantity of this constituent in the rainwater at Agricultural College, Mississippi, for the years 1894 and 1895 is here mentioned. With an average yearly rainfall of 44.11 inches for the two years the soil is reported to have received per acre, annually, 2.35 pounds of ammoniacal nitrogen and 0.73 pound of nitrate nitrogen.

While the total nitrogen found in the rainwater varies considerably, certain observations have been made which seem to be quite generally true throughout the world. The ammoniacal nitrogen is found to be in excess of the nitrate nitrogen. The former fluctuates from year to year and from month to month, while the latter remains more constant throughout the year, being slightly higher during the summer season. Summer rains have been found to contain more nitrogen than winter rains and snow less nitrogen than rainwater. The precipitation determines very largely the total amount of nitrogen supplied to the soil. Wind, electrical discharges and other meteorological conditions appear to have but little effect on the quantity of oxidized nitrogen in the rainwater. These latter generalizations, however, are not in accord with the findings of Masson (6), working in Australia, who reports that the total oxidized nitrogen found in the rainwater accompanying a storm depends upon the type of weather and is practically independent of the amount of rainfall, and that the concentration of oxidized nitrogen varies inversely with the amount of precipitation.

In order to determine the quantity of nitrogen in the precipitation at Ithaca, New York, analyses of the rainwater have been made for a number of years and the results that have been obtained are herein reported.

COLLECTIONS OF RAINWATER

Collections of the rainwater were begun in August, 1914, and are continued at the present time. Monthly examinations have been made for ammoniacal

and nitrate nitrogen and from the quantity of water collected by months, the yearly precipitations have been determined. The rain and snow are collected in a metal rain-gauge 8 inches in diameter which stands about 9 feet from the ground and which is protected from birds by a movable frame projecting a little above and beyond the top of the gauge. The latter is located in a field near which there are no factories and as this area is almost continually under cultivation or covered with snow the air is comparatively free from smoke and dust. A railroad running about one-half mile to the south and a small heating plant located about one-half mile to the west of the field, undoubtedly, at certain times, contaminate the air to some extent.

The rain-gauge is emptied after each rain or snow and its contents stored in glass bottles, which contain a few drops of mercuric chloride solution, until the first of each month when the water is measured, filtered when necessary to remove any insects or wind blown material and the nitrogen determined.

ANALYSIS OF THE RAINWATER

The samples of rainwater are analyzed for ammoniacal nitrogen by the Nessler reaction as used in water analysis and for nitrate nitrogen by the phenol-disulfonic-acid method. Organic nitrogen is not determined. When present in the rainwater it is believed to be largely due to contamination from foreign particles existing temporarily in the atmosphere near the surface of the earth and a more accurate value for the nitrogen actually brought down by the rain is probably obtained by disregarding it.

NITROGEN IN THE RAINWATER

The results reported are for the ammoniacal and nitrate nitrogen content of the rainwater from August 1, 1914 to May 1, 1920. As the nitrogen in the rainwater for May, June and July for the experimental year 1914–1915 was not determined, this discussion will be confined to the nitrogen in the rainwater for a period of five years beginning May 1, 1915 and ending May 1, 1920.

The quantity of nitrogen found in the rainwater for each month of the several years is presented in tables 1 to 6, inclusive, together with the corresponding monthly precipitation. The data given in table 1 cover a period of only 9 months, and as the rainfall is comparatively large for the three months not tabulated these data are not included in table 7 in which the results for the period mentioned above are brought together. It may be seen from this latter table that with an average rainfall of 29.31 inches, the soil received an average yearly supply of 12.51 pounds of nitrogen to the acre, 11.5 pounds of which were ammoniacal nitrogen and 1.01 pounds of which were nitrate nitrogen. This value for the ammoniacal nitrogen is much greater than the values generally ascribed to it. At Rothamsted, England, where the average annual rainfall for 28 years was slightly less than the one reported above, only 2.64

pounds of ammoniacal nitrogen were found. The value for the nitrate nitrogen is in close agreement with the values found by other workers.

The articles reviewed by Miller (7) show the total nitrogen found in the rainwater of thirty different localities to vary from 19.91 pounds to 1.63 pounds per acre yearly. The largest amount was found in the rainwater at Proskau, Germany, while the smallest quantity was found in that of Lincoln, New Zealand. The total nitrogen found in the precipitation for the five years reported at Ithaca, as may be seen in table 7, lies about midway between these two extremes.

It is quite evident from the accompanying figure, in which the results given in table 7 are shown graphically, that the ammoniacal nitrogen fluctuates from

TABLE 1

Nitrogen in the rainwater between August 1, 1914, and May 1, 1915

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm.*	*lbs.*
August, 1914	5.58	3.82	0.38	1.15
September	1.98	0.96	0.07	0.28
October	1.13	0.61	0.08	0.19
November	0.98	1.13	none	0.31
December	1.94	1.17	none	0.32
January, 1915	5.20	2.10	none	0.58
February	1.19	1.11	none	0.31
March	0.27	0.38	none	0.10
April	0.73	5.83	0.43	1.72
Total 9 months	19.00	17.11	0.96	4.96

TABLE 2

Nitrogen in the rainwater between May 1, 1915, and May 1, 1916

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm.*	*lbs.*
May, 1915	2.31	6.04	0.73	1.86
June	2.85	9.12	none	2.51
July	6.34	20.28	none	5.58
August	3.24	6.72	none	1.84
September	2.39	6.89	none	1.89
October	3.83	1.91	none	0.53
November	1.01	0.47	0.16	0.17
December	2.07	1.49	0.60	0.57
January, 1916	0.17	0.22	0.17	0.11
February	2.31	1.05	0.43	0.41
March	1.47	1.08	none	0.30
April	2.33	4.36	0.68	1.39
Total for year	30.32	59.63	2.77	17.16

TABLE 3

Nitrogen in the rainwater between May 1, 1916, and May 1, 1917

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm.*	*lbs.*
May, 1916	3.72	12.39	none	3.40
June	3.35	12.21	none	3.36
July	2.67	14.88	none	4.09
August	1.77	3.60	0.22	1.05
September	5.71	3.47	none	0.95
October	1.45	2.31	none	0.64
November	1.45	0.93	0.54	0.40
December	1.00	7.25	0.30	2.08
January, 1917	1.12	1.97	0.33	0.63
February	0.27	0.79	0.14	0.26
March	1.08	2.66	0.84	0.96
April	1.81	5.79	1.28	1.94
Total for year	25.40	68.25	3.65	19.76

TABLE 4

Nitrogen in the rainwater between May 1, 1917, and May 1, 1918

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm.*	*lbs.*
May, 1917	3.98	12.70	0.89	3.74
June	7.11	14.79	1.46	4.48
July	2.94	15.04	0.77	4.35
August	8.30	7.96	1.23	2.53
September	2.31	0.92	none	0.25
October	4.66	2.17	0.55	0.75
November	0.41	0.80	0.09	0.24
December	0.68	0.18	none	0.05
January, 1918	0.68	0.81	0.10	0.25
February	0.99	1.08	0.54	0.45
March	1.56	0.67	none	0.18
April	2.88	1.47	0.36	0.50
Total for year	36.50	58.59	5.99	17.77

TABLE 5

Nitrogen in the rainwater between May 1, 1918, and May 1, 1919

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm.*	*lbs.*
May, 1918	5.06	0.71	0.75	0.40
June	2.98	0.82	none	0.23
July	4.16	3.45	none	0.95
August	3.48	1.84	0.48	0.64
September	5.73	1.65	none	0.45
October	2.50	0.54	0.37	0.25
November	0.89	0.28	0.20	0.13
December	0.55	0.26	none	0.07
January, 1919	0.79	0.42	0.47	0.24
February	0.70	0.34	0.30	0.18
March	1.52	0.97	none	0.27
April	1.93	0.84	0.50	0.37
Total for year	30.29	12.12	3.07	4.18

TABLE 6

Nitrogen in the rainwater between May 1, 1919, and May 1, 1920

MONTH COLLECTED	RAINFALL	N AS NH_3	N AS NO_3	N PER ACRE
	ins.	*mgm.*	*mgm*	*lbs.*
May, 1919	4.82	1.54	0.63	0.60
June	1.82	0.70	0.37	0.30
July	3.27	0.88	0.70	0.43
August	1.31	0.22	0.49	0.20
September	1.47	0.56	none	0.15
October	2.82	0.72	none	0.20
November	2.22	0.50	none	0.14
December	0.76	0.49	none	0.13
January, 1920	0.92	0.19	none	0.05
February	0.69	0.77	0.13	0.24
March	1.37	1.67	0.26	0.53
April	2.56	2.29	0.29	0.71
Total for year	24.03	10.53	2.87	3.68

TABLE 7

Nitrogen in the rainwater between May 1, 1915, and May 1, 1920

MONTH COLLECTED	RAINFALL	N AS NH_3 PER ACRE	N AS NO_3 PER ACRE	TOTAL N PER ACRE
	ins.	*lbs.*	*lbs.*	*lbs.*
May	19.89	9.18	0.82	10.00
June	18.11	10.37	0.51	10.88
July	19.38	15.00	0.40	15.40
August	18.10	5.59	0.67	6.26
September	17.61	3.70	none	3.70
October	15.26	2.11	0.26	2.37
November	5.98	0.82	0.27	1.09
December	5.06	2.66	0.24	2.90
January	3.68	0.99	0.29	1.28
February	4.96	1.11	0.43	1.54
March	7.00	1.94	0.30	2.24
April	11.51	4.06	0.85	4.91
Total	146.54	57.53	5.04	62.57
Yearly average	29.31	11.50	1.01	12.51

month to month while the nitrate nitrogen remains fairly constant and that the total nitrogen depends very largely on the amount of rainfall. While it is generally true that with a large precipitation the ammoniacal nitrogen is correspondingly large, there is a consistent falling off in this form of nitrogen with the month of August, and it continues to decrease in spite of the usual heavy rainfall during this and the following two months. This decrease in the amount of ammoniacal nitrogen may be due to the fact that the heavy rains of the late spring and early summer have washed the greater portion of the ammonia from the atmosphere. It has been observed by Shutt and Dor-

rance (10) that continued rains free the atmosphere of nitrogen and that a short shower usually shows higher nitrogen concentration than a longer one. An inspection of tables 2 to 6, inclusive, will show this falling off in the ammoniacal nitrogen to occur for each of the five years reported.

As the rainwater was analyzed only monthly it is impossible to state the effect of electrical discharges on its nitrate nitrogen content. Table 7 shows the nitrates to be somewhat higher in the rainwater of the spring and summer months than they are during the remainder of the year and since they are found to be highest during the time of the most frequent electrical storms it is possible that some of the nitrate nitrogen present is the result of the oxidation of other forms of nitrogen existing in the atmosphere. This table also shows very much more nitrogen to be brought down in the summer rain than in the winter precipitation. The rain falling during May, June, July and August contained 67.88 per cent of the total nitrogen brought down in the rainwater between May 1, 1915, and May 1, 1920.

The relatively high amount of ammoniacal nitrogen found in the rainwater at Ithaca can not be attributed to contamination, as the air is unusually free of dust and smoke. The greatest source of contamination is probably from the soil particles blown about in the immediate vicinity of the rain-gauge. As previously stated a railroad and a heating plant, both of which are located about one-half mile from the rain-gauge undoubtedly increase the ammonia in the rainwater at certain times. These sources of contamination, however, could not account for the consistent differences in the amounts of ammonia in the rainwater for the months of July and August and in all probability furnish only a very small portion of the total quantity of this constituent found to be present in the yearly precipitations.

SUMMARY

With an average yearly rainfall of 29.31 inches between May 1, 1915, and May 1, 1920, the soil received annually 12.51 pounds of nitrogen to the acre. Of this amount 11.5 pounds was in the form of ammoniacal nitrogen and 1.01 pounds in the form of nitrate nitrogen.

The ammoniacal nitrogen was found to fluctuate from month to month and from year to year while the nitrate nitrogen remained more constant. The amount of total nitrogen in the rainwater was to a large extent dependent on the amount of rainfall, a high nitrogen content accompanying a correspondingly high precipitation.

The rainfall during the spring and summer months contained more nitrogen than the rain falling during the other two seasons of the year. The ammoniacal nitrogen decreased rather suddenly during August and continued low during September and October in spite of heavy rainfalls. This decrease was probably due to the atmosphere being washed comparatively free of ammonia by previous rains.

Electrical discharges did not increase the nitrate nitrogen content of the rainwater to any considerable extent.

The amount of ammoniacal nitrogen brought down in the rain falling at Ithaca, New York, is somewhat larger than that reported to be present in many parts of the world, while the nitrate nitrogen content is about the same.

REFERENCES

(1) CROWTHER, C., AND RUSTON, A. G. 1911 The nature, distribution and effects upon vegetation of atmospheric impurities in and near an industrial town. *In* Jour. Agr. Sci., v. 4, p. 25–55.

(2) VON FEILITZEN, HJALMAR, AND LUGNER, IVAR 1910 On the quantity of ammonia and nitric acid in the rain water collected at Flahult in Sweden. *In* Jour. Agr. Sci., v. 3, p. 311–313.

(3) HUDIG, J. 1912 The amounts of nitrogen as ammonia and nitric (and nitrous) acid in the rainwater collected at Uithuizermeeden, Gronigen. *In* Jour. Agr. Sci., v. 4, p. 260–269.

(4) JURITZ, C. F. 1914 Chemical composition of rain in the Union of South Africa. *In* So. Afric. Jour. Sci., v. 10, p. 170–193. *Abs. in* Jour. Chem. Soc. (London), v. 106, no. 1, p. 916.

(5) KNIGHT, NICHOLAS 1911 Nitrogen in rain and snow. *In* Proc. Iowa Acad. Sci., v. 18, p. 75–77.

(6) MASSON, O. 1916 The influence of weather conditions upon the amounts of nitrogen acids in the rainfall and atmosphere in Australia. *In* Rpt. Brit. Assoc. Adv. Sci., v. 86, p. 128–130.

(7) MILLER, N. H. J. 1905 The amounts of nitrogen as ammonia and as nitric acid and of chlorine in the rain water collected at Rothamsted. *In* Jour. Agr. Sci., v. 1, p. 280–303.

(8) RUSSELL, E. J., AND RICHARDS, E. H. 1919 The amount and composition of rain falling at Rothamsted. *In* Jour. Agr. Sci., v. 9, p. 309–337.

(9) SHIPLEY, J. W. 1919 Ammonia and nitrous nitrogen in the rainwater of Southwestern Alaska. *In* Ohio Jour. Sci., v. 19, p. 230–234.

(10) SHUTT, F. T., AND DORRANCE, R. L. 1917 The nitrogen compounds in rain and snow. *In* Proc. and Trans. Roy. Soc. Canada, v. 11, no. 3, p. 63–71.

(11) TRACY, S. M. 1895 Ammonia in rain water. *In* Miss. Agr. Exp. Sta. 8th Ann. Rpt., p. 102.

(12) TRIESCHMANN, J. E. 1919 Nitrogen and other compounds in rain and snow. *In* Chem. News, v. 119, p. 49.

A SHORT TEST FOR EASILY SOLUBLE PHOSPHATE IN SOILS[1]

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Received for publication December 16, 1920

INTRODUCTION

A large amount of work has been done on the digestion of soils with weak solvents, especially acids, in attempts to separate the easily soluble plant-food constituents from the less-soluble portions. The one kind is generally called easily soluble, available or active, and the other dormant, non-available, or, preferably, potential plant-food. This has come about as a result of efforts made to devise somewhat arbitrary methods for measuring that portion of the plant-food in soils which can be utilized by crops at the present time as distinguished from the remainder which in all probability will become more slowly available in the future.

HISTORICAL

Numerous methods have been devised for the above purpose and frequently the results obtained by different forms of procedure do not agree; consequently, there has arisen considerable discussion among scientific workers interested in this subject as to the value of such methods for the purpose intended, which has divided them into two general groups. One comprises those who believe that, on account of it being impossible to duplicate soil conditions in the laboratory by the use of arbitrary chemical methods, no credence can be placed in work of this character. To support this they cite the fact that the results obtained by such methods often vary widely among themselves. There are also some among this class who not only take the position that these methods have no significance, but maintain that all chemical methods, including those for the estimation of total plant-food constituents, give no reliable data for indicating the productive capacity of soils. The other group, while conceding the above to be partly true, nevertheless contend that some of the methods, although they may have their limitations, do give results of a certain value when used by workers with sufficient experience who know how to interpret them in connection with other data that may be obtained. For this reason they continue to employ them in their work.

[1] Published by permission of the director of the Kentucky Agricultural Experiment Station.

[2] The author desires to thank Dr. A. M. Peter, head of the department of chemistry, for helpful criticism in the preparation of this manuscript.

It is not necessary to discuss the relative merits of these opposite views or to include a summary of all the work that has been done, as the references in the literature pertaining to this subject are very numerous. For this reason only those which refer to certain matters discussed here will be mentioned.

During the progress of the work given in tables 2 to 5, an article came to the attention of the writer describing some work by Russell and Prescott of the Rothamsted Experiment Station (5), who have made rather extensive experiments on the determination of phosphorus in weak acid digestions of soils. Their work has been confined to a study of this element and among other things includes its adsorption by the soil and the effect of time of digestion and different strengths of various acids on the results obtained. While their experiments are somewhat different from those employed in this work, it is of interest to note that their results show that a short digestion with some acids, especially nitric, not exceeding a certain strength, puts more phosphorus into solution than does one for a longer time. This they prove to be due to adsorption. On account of the different methods of procedure and the limited number of soils used in their work, the conclusions reached regarding the behavior of nitric acid have been only partly confirmed here. An excellent summary of some previous investigations on adsorption phenomena in soils is given by these writers and in a resumé by Prescott (4).

Of all the methods that have been proposed for the estimation of easily soluble constituents in soils, probably the most widely used in this country are those involving the digestion of the soil with weak acids, either 0.2*N* hydrochloric or nitric, for a limited time at a definite temperature. The former was first adopted by the Association of Official Agricultural Chemists as a provisional method and included in their Methods of Analysis (3, p. 18).

Probably the first work with 0.2*N* nitric acid as a solvent for plant-food in soils was done by Dr. A. M. Peter, at this station, and the results were so favorable that it was proposed for trial to the association. Later, a committee appointed for the purpose of editing and revising their methods of analysis recommended it as a tentative method to replace the weak hydrochloric digestion (1, p. 27). It should be stated, however, that the method as recommended differs materially in some respects from the procedure as carried on here.

The last committee appointed by the association for the revision of methods has failed, for some unaccountable reason, to include any method for the above separations; consequently none appears in the latest revised Methods of Analysis of the association (2).

EXPERIMENTAL

In the early part of 1916, the writer, while engaged in some work on the digestion of soils with 0.2*N* nitric acid and other weak solvents, observed that adsorption apparently had considerable influence on the results obtained,

especially in the phosphorus determinations. It was found at that time (in some unpublished work) that in the 0.2*N* nitric acid digestion, when equal volumes of the acid were used on different amounts of soil, the smaller weight of soil showed more phosphorus in solution after the digestion, in proportion to the quantity of soil used, than was to be expected. An explanation which suggested itself at the time was that where the smaller mass was used, its adsorptive capacity was not satisfied under the conditions of the experiment, but when a larger amount of the same was in contact with the richer solution of phosphate, this requirement was more nearly met. It is possible, however, that the smaller mass of soil allows its particles to be exposed more completely to the relatively larger volume of acid and that this partly accounts for the discrepancies. The results obtained are given in table 1.

TABLE 1

Phosphorus dissolved by 1500 cc. of 0.2 N HNO_3 *from different weights of soil, after 5 hours' digestion,* being shaken every 30 minutes*

SOIL NUMBER	PHOSPHORUS OBTAINED FROM		RATIO
	7.5 gm. of soil	150 gm. of soil	1:20
	gm.	*gm.*	
56525	0.0003	0.0010	1:3.3
56526	0.0010	0.0059	1:5.9
56528	0.0008	0.0020	1;2.5
56530	0.0003	0.0009	1:3.0
14604	0.0327	0.4303	1:13.2
14606	0.0005	0.0026	1:5.2
56527	0.0003	0.0011	1:3.7
56529	0.0002	0.0005	1:2.5
56531	0.0003	0.0016	1:5.3
56532	0.0002	0.0004	1:2.0

* These digestions were made at room temperature, as were all others described in this paper.

A large excess of free nitric acid was present at the end of the digestion, in every experiment. That the solvent power of the acid for phosphate was not satisfied is apparent from the large amount of phosphorus taken up from soil no. 14604, as compared with that dissolved from the other soils. It should be borne in mind that the neutralizing power of our soils for 0.2*N* nitric acid, under the conditions of these experiments, is practically negligible except when carbonate is present. Assuming that the action was only that of an acid on the soil with no subsequent fixation of the dissolved phosphate, and that the soil surfaces exposed were somewhat in proportion to the amounts of soil used, the ratio of the phosphorus dissolved would be expected to be more comparable to the relative amounts of soil present. The ratio of the latter was constant (1:20) while that of the former varied considerably in individual soils, the maximum being 1:13.2 and the minimum 1:2. In other

words, the last ratio indicates in these particular soils where the larger amounts were used, only about one-tenth of the quantity of phosphorus in solution that would be expected, provided no adsorption or other interfering factors had intervened.

After the foregoing experiments were completed, attempts were made to determine if adsorption in soils was exerting any considerable influence on the amounts of plant-food constituents obtained in the weak acid digestion. In order to demonstrate this point, digestions were made of the same amounts of soil for short and longer periods of time and it was found that short digestions—for instance, 5 minutes—in 0.02*N* HNO_3, with shaking every minute, gave higher results with some soils as regards certain constituents, especially phosphorus, than the prescribed 5-hour period, with shaking every 30 minutes. In fact, in some soils, by placing them on folded filters, pouring the acid on and allowing it to filter immediately, the results compared favorably with the longer contact. This, however, did not hold true with all soils.

The above work comprises part of an investigation that is being carried on by the writer in an effort to obtain, if possible, more definite knowledge concerning the effect of weak acid digestions of our soils regarding certain constituents, namely phosphorus, potassium, calcium and silica. That such digestions, especially for short intervals of time, do have a certain value for indicating the productive capacity of a soil, is believed for the following reasons. First, the short, weak acid digestion largely eliminates the time action of the acid on the soil and this is one objection that has been raised against all methods of this character; second, the error due to adsorption by the soil, especially if it is of a gradual nature, is partly eliminated; third, the soil silicates are not appreciably attacked, as shown by the silica obtained in the digestion and finally a comparison of the short and the long digestions shows that about the same amount of calcium, a large bulk of the potassium and, in many cases, as much phosphorus is obtained in the former. The inference is that the amounts so obtained are more loosely held and in all probability are combined with the organic matter or humus portions of the soil rather than with the mineral silicates. As stated before, however, this work is being continued and a publication will probably be issued in the near future.

During the last few years the number of soils sent in by our farmers for tests as to their fertilizer requirements has been increasing to such an extent that short qualitative tests have been resorted to in answer to these demands. One of the tests generally made on such samples is for total phosphorus, for the reason that it is one of the most deficient elements in our soils. Unfortunately, however, the test for easily soluble phosphorus requires more time and quantitative work. Therefore it was thought that if some short test could be developed for finding out something about the amount of this element taken up in weak acid, it would be of some benefit in arriving at the need of the soil for soluble phosphate, when considered in connection with the total amount present.

As the short digestion gave as good results with a large number of soils as the longer, the following test, among others, was tried:

Ten grams of air-dried soil was added to 25 cc. of 0.2*N* HNO_3 and the whole shaken every minute for 5 minutes. The solution was filtered until clear into a $\frac{3}{4}$ by 6 inch test tube, 1 or 2 cc. of 60 per cent NH_4NO_3 solution was then added, and 5 cc. of ordinary molybdate solution as prescribed in the official method for fertilizers (3, p. 2). The contents of the test tube were heated to about 60°C., shaken several times and allowed to stand about 30 minutes at room temperature.

A possible objection may be raised against a method of this kind. Since it is only a qualitative test, how are the results obtained by it to be described to an inexperienced worker so that he can interpret them when made? In answer to this it might be stated that those given in the following tests were made by the writer without any previous experience and none have been changed or discarded.

The results mar ed "large," "fair," "moderate," "very moderate," etc., stand in decreasing order of the amount of ammonium phospho-molybdate obtained. These terms are only approximately defined and in some instances may be partly interchangeable without seriously vitiating the interpretation of the test. Although difficult to describe exactly, the term "moderate" indicates that the yellow precipitate, after settling by gentle tapping of the tube, occupied an area in the rounded tip from 0.5 to about 0.75 cm. in diameter.[3] After a little experience no great difficulty will be found in the relative terms to be applied for purposes of comparison.

After the short tests were all made, the results were compared with the quantitative results from 5-hour digestions, so that no preconceived judgement might be formed about the terms to be applied. As stated above, none were changed or discarded.

The 0.2*N* HNO_3 digestion was made by digesting the soil in the proportions of 1 gm. of soil to 10 cc. 0.2*N* HNO_3 for 5 hours at room temperature, shaking every 30 minutes. It was then filtered and an aliquot evaporated to dryness. More HNO_3 was added to oxidize the organic matter, it was again evaporated and the last traces of HNO_3 eliminated by evaporation with HCl. The residue was dried on a steam bath to dehydrate SiO_2, taken up with HCl and H_2O, filtered and the phosphorus determined with ammonium molybdate by precipitating at 40°C. in a small volume and allowing the yellow precipitate to stand at the above temperature for an hour or so and finally over-night at room temperature. It was then filtered and determined volumetrically.

The total phosphorus was determined by the magnesium-nitrate method with slight modifications (1, p. 25).

The large majority of determinations of total and 0.2*N* HNO_3-soluble phosphorus were made by the writer. The remainder were made by different

[3] The average diameter of 10 precipitates of this character was 0.64 cm.

analysts in the regular soils work. Where comparisons have been made of virgin with the corresponding cultivated soil, the work was carried on at the same time. The numbers for these are bracketed in the tables.

The soils used in the work have been divided into four general groups. While the classifications are somewhat arbitrary and not definite in all cases, they are satisfactory for the purpose. The results obtained by the short test and the comparisons with the other determinations are given in tables 2, 3, 4 and 5.

TABLE 2

Determinations on soils in which the amounts of total and easily soluble phosphorus are small

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
25002	Cultivated	0.037	None	0.0008
25004	Virgin	0.050	Trace	0.0015
56447	Cultivated	0.043	None	0.0010
56449	Virgin	0.079	Very small	0.0021
56489	Virgin	0.031	None	0.0006
56490	Cultivated	0.019	None	0.0006
56491	Virgin	0.018	None	0.0006
56492	Cultivated	0.019	None	0.0006
56493	Virgin	0.049	Trace	0.0014
56495	Cultivated	0.042	None	0.0008
25662	Cultivated	0.062	None	0.0009
25663	Virgin	0.072	Trace	0.0015
56497	Cultivated	0.047	Trace	0.0015
56499	Virgin	0.037	Very small, larger than 56497	0.0023
36263	Virgin	0.030	Trace	0.0009
43527	Cultivated	0.048	None	0.0004
56699	Cultivated	0.050	None	0.0011
50117	Cultivated	0.044	Trace	0.0016
56701	Cultivated	0.024	None	0.0006
56702	Cultivated	0.037	Trace	0.0014
43506	Cultivated	0.052	Trace	0.0007
56457	Cultivated	0.030*	None	Not determined
56458	Virgin	0.033*	None	Not determined
56485	Virgin	0.032*	None	Not determined
56487	Cultivated	0.021*	None	Not determined

TABLE 2—*Continued*

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
43526	Cultivated	0.042	Trace	0.0013
56652	Cultivated	0.027	None	0.0005
56740	Cultivated	0.031	None	0.0006
56584	Cultivated	0.022	Very small	0.0016
56741	Cultivated	0.032	None	0.0007
56586	Cultivated	0.055	Very small	0.0012
56525	Cultivated	0.018	None	0.0007
56529	Cultivated	0.020	None	0.0010
56530	Cultivated	0.026	Trace	0.0014
56531	Cultivated	0.020	Very small	0.0013
56532	Cultivated	0.030	None	0.0011
56587	Cultivated	0.041	None	0.0013
56592	Cultivated	0.064	Trace	0.0009
25424	Cultivated	0.053	Very small	0.0014
25459	Cultivated	0.021	None	0.0004
25454	Cultivated	0.024	None	0.0002
25418	Cultivated	0.031	None	0.0006
25224	Cultivated	0.053	Trace	0.0006
17902	Cultivated	0.028	None	0.0002
25020	Cultivated	0.054	None	0.0003
36453	Cultivated	0.040*	Trace	Not determined
36538	Virgin	0.074	Trace	0.0026
36539	Cultivated	0.052	None	0.0011
Average of 43 soils.....		0.040		0.0010†

* Not included in average.

† That is, 2.5 per cent of the total P.

TABLE 3

Determinations on soils in which the total amount of phosphorus is small, but the amount of easily soluble phosphorus is comparatively large

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
36694	Cultivated	0.068	Very small	0.0043
36696	Virgin	0.091	Very small, more than 36694	0.0051
36792	Virgin	0.088	Trace, more than 36796	0.0028
36796	Cultivated	0.067	Trace	0.0017
56549	Cultivated	0.043	Trace	0.0028
56583	Cultivated	0.059	Moderate	0.0043
56700	Cultivated	0.053	Trace	0.0021
56526	Cultivated	0.027	Very moderate	0.0022

TABLE 3—*Continued*

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
56528	Cultivated	0.026	Small	0.0022
56588	Cultivated	0.039	Very small	0.0019
25227	Cultivated	0.049	Very small	0.0017
36510	Cultivated	0.070	Moderate	0.0149
36511	Cultivated	0.067	Moderate, less than 36510	0.0114
36687	Cultivated	0.087	Very moderate	0.0079
56188	Cultivated	0.080	Very moderate	0.0060
56501	Cultivated	0.070	Moderate	0.0109
56503	Virgin	0.074	Moderate, more than 56501	0.0125
25796	Cultivated	0.081	Very small	0.0031
25797	Virgin	0.092	Small	0.0074
Average of 19 soils.....		0.065		0.0055*

* That is, 8.5 per cent of the total P.

TABLE 4

Determinations on soils in which the total amount of phosphorus is large but the amount of easily soluble phosphorus is comparatively small

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
*9768	Virgin	0.142†	Very moderate, larger than 9771	0.0062†
9771	Cultivated	0.083	Very small	0.0019
14411	Cultivated	0.165	Trace	0.0036
Same			Trace	
*14412	Virgin	0.199†	Moderate, much larger than 14411	0.0191†
Same			Same	
56959	Virgin	0.188	None	0.0024
56960	Cultivated	0.129	None	0.0018
56742	Cultivated	0.088	None	0.0010
56527	Cultivated	0.077	None	0.0010
56585	Cultivated	0.079	Very small	0.0018
36957	Cultivated	0.111	Trace	0.0009
36775	Cultivated	0.114	Trace	0.0024
25114	Cultivated	0.157	Trace	0.0046
17287	Cultivated	0.142	Very small	0.0028

* These soils belong in table 4 and are included here for comparison with the cultivated.
† Not included in average.

TABLE 4—*Continued*

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
25910	Cultivated	0.101	None	0.0008
17285	Cultivated	0.136	Very small	0.0038
43563	Cultivated	0.112	Trace	0.0011
17480	Cultivated	0.094	Trace	0.0015
17481	Cultivated	0.127	Very small	0.0030
36798	Cultivated	0.144	Trace	0.0019
25362	Cultivated	0.103	Trace	0.0006
25228	Cultivated	0.095	Very small	0.0017
25134	Cultivated	0.107	Trace	0.0009
25135	Cultivated	0.107	None	0.0008
25995	Cultivated	0.093	None	0.0007
25311	Cultivated	0.131	None	0.0012
36688	Cultivated	0.134	Small	0.0031
56322	Cultivated	0.138	None	0.0022
56324	Cultivated	0.139	None	0.0016
56325	Cultivated	0.136	None	0.0010
43002	Cultivated	0.122	Trace	0.0014
36574	Cultivated	0.144	None	0.0010
14956	Cultivated	0.174	Trace	0.0014
2306	Cultivated	0.154	Very small	0.0023
Average of 31 soils.....		0.123		0.0018‡

‡ That is, 1.5 per cent of the total P.

TABLE 5

Determinations on soils in which the amounts of total and easily soluble phosphorus are large

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
17483	Cultivated	0.175	Moderate	0.0158
17485	Virgin	0.190	Moderate, less than 17483	0.0122
2305*	Cultivated	0.204	Fair, much larger than 2306	0.0145
2306†	Cultivated	0.154‡	Very small	0.0023‡
56747	Virgin	0.317	Large	0.0780
Same			Same	
56784	Cultivated	0.151	Fair, much less than 56747	0.0234
Same			Same	
56733	Cultivated	0.427‡	Moderate	Not determined
50592	Cultivated	0.620	Large	0.2260

* Cultivated since 1884.

† Cultivated since 1860, same farm. Belongs to table 3 but included here for comparison with 2305.

‡ Not included in average.

TABLE 5—*Continued*

SOIL NUMBER	CHARACTER	TOTAL P	SHORT TEST	P DETERMINED AFTER 5 HOURS' DIGESTION IN 0.2 *N* HNO_3
		per cent		*per cent*
36790	Cultivated	0.791	Large	0.4200
25203	Cultivated	1.464	Large	0.6180
25204	Cultivated	2.227	Large	0.9600
25112	Cultivated	0.243	Moderate	0.0176
25039	Cultivated	0.205	Moderate	0.0160
50735	Cultivated	0.254	Moderate	0.0165
43407	Cultivated	0.203	Moderate	0.0171
25824	Cultivated	0.207	Moderate	0.0116
56329	Cultivated	0.148	Very moderate	0.0067
56855	Cultivated	0.107	Moderate	0.0111
25664	Cultivated	0.093	Very moderate	0.0072
25295	Cultivated	0.101	Moderate	0.0090
56188	Cultivated	0.080	Very moderate	0.0060
9768	Virgin	0.142	Very moderate	0.0062
14412	Virgin	0.199	Moderate	0.0191
Average of 21 soils.....		0.387		0.1196§

§ That is, 30.9 per cent of the total P.

GENERAL DISCUSSION AND CONCLUSIONS

Assuming that the 0.2*N* HNO_3 method has some value, the question arises, where should the demarcation in the results come when they are to be interpreted as to the probable need of a soil for soluble phosphate. After considerable experience from a study of a large number of our soils, it is the writer's opinion that a soil should show a minimum phosphorus solubility of 0.005 per cent by this method, regardless of the total amount present. Between the range of 0.005 and 0.0075 per cent the use of phosphate may be beneficial, while above this it is probably not required.

In regard to total phosphorus, it might be stated that any soil below 0.08 or 0.10 per cent is in need of phosphate, between these figures and 0.15 per cent it may respond, and above this it is probably not necessary. However, this arbitrary classification as to the total probably depends to a large extent on its availability in the soil.

From an examination of the tables we find, therefore, that the demarcation in the results by the short test is defined by "very moderate" to "moderate." As stated above, these terms are difficult to define in some cases and in these instances may be partly interchangeable. At the time, it was the writer's judgment that the terms "moderate," "fair" or "large" indicated that no phosphate was needed, and "very moderate" that there was a doubt, and below this it was necessary. With but few exceptions it will be found that the results are in agreement with those of the 5-hour digestion. The exception may be due partly to inexperience with the tests at first, making it difficult

to define every one accurately, inasmuch as none were changed or discarded. Again, some of the variations are due to differences in the solubility of the phosphate in short and in longer periods of time, partly caused by subsequent adsorption.

The short test probably could be applied for calcium and potassium if desired, and although no attempts have been made, it is possible that by the employment of suitable apparatus and perhaps some modification in the procedure, an approximate quantitative determination could be made of phosphorus and possibly other elements which could be correlated with the figures obtained in the long digestion.

It will be observed that there are considerable differences in the behavior of soils in the weak acid digestion, and the percentages of the total phosphorus soluble in the weak acid are widely divergent. Assuming the surface $6\frac{2}{3}$ inches to weigh 2,000,000 pounds, the averages obtained in the different groups are as given in table 6.

There is no doubt that the conclusions reached by the $0.2N$ HNO_3 digestion are in accord with what we know about the soils in tables 2 and 4. Those in

TABLE 6

	TOTAL P		0.2 *N* HNO_3 SOLUBLE P		PER CENT OF THE TOTAL P SOLUBLE IN 0.2 *N* HNO_3
	Per cent	Pounds per acre	Per cent	Pounds per acre	
Table 2.....	0.040	800	0.0010	20	2.5
Table 3.....	0.065	1300	0.0055	110	8.5
Table 4.....	0.123	2460	0.0018	36	1.5
Table 5.....	0.387	7740	0.1196	2392	30.9

table 2 show need of phosphate and respond to phosphate treatment in the field. They represent a large majority of our soils of different types and experimental field results verify the laboratory tests. The phosphate in such soils is low, not available and is probably combined with iron and aluminum. On the contrary, the soils in table 5 represent some of our best; those which are in the blue-grass region. Many of these soils have a large content of calcium phosphate and the better class do not respond to phosphate treatment. Here again the $0.2N$ HNO_3 digestion is in accord and also the short test. The soils in tables 3 and 4 represent those regarding which any method for availability would have decided practical value. The weak acid digestion apparently discriminates between those soils in which the phosphorus exists as calcium phosphate and those where it is combined in other forms such as iron and aluminum and generally considered as not available.

The experimental field results in this state show that on those soils which need phosphate, applications of limestone and acid phosphate or rock phosphate give the best results. As the phosphate in either case is probably maintained in the soil in the form of calcium phosphate which, if true, would

more than likely be shown by the 0.2*N* HNO_3 digestion as indicated by some of the foregoing results, this shows that the weak acid digestion should have some value in practice. In fact, those who have been engaged in the chemical analysis of soils at the Kentucky station in the past, before any experimental fields were established, predicted those areas which would respond to phosphate treatment and it is with some gratification that they now find these predictions confirmed.

REFERENCES

(1) Association of Official Agricultural Chemists, Alsberg, C. L., Chairman of Board of Editors 1916 Report of the committee on editing methods of analysis. *In* Jour. Assoc. Off. Agr. Chem., v. 1, no. 4 (sup.), p. 1–57.

(2) Association of Official Agricultural Chemists, Doolittle, R. E., Chairman of the Committee on Revision of Methods 1920 Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Published by the Association, Washington, D. C.

(3) Association of Official Agricultural Chemists, Wiley, H. W., Editor 1908 Official and provisional methods of analysis. U. S. Dept. Agr. Bur. Chem. Bul. 107 (rev.).

(4) Prescott, J. A. 1916 The phenomenon of absorption in its relation to soils. *In* Jour. Agr. Sci., v. 8, pt. 1, p. 111–130.

(5) Russell, E. J., and Prescott, J. A. 1916 The reaction between dilute acids and the phosphorus compounds of the soil. *In* Jour. Agr. Sci., v. 8, pt. 1, p. 6–110.

THE FORMS OF NITROGEN IN SOYBEAN NODULES[1]

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Received for publication December 10, 1920

The forms of nitrogen present in the root nodules of legumes have been the source of much speculation. From the results of many experiments, it is known that the production of root nodules may be followed by a decided gain in the total nitrogen of the plant, but the initial form of nitrogen assimilated by bacteria is unknown. Also the nature of the nitrogenous substance or substances assimilated by the higher plant remains an unsolved problem. Perhaps the cells of the bacteria are absorbed directly by the plant, or more probably these cells are first acted upon by enzymes and thus prepared for plant metabolism. The results of chemical studies of nodules may throw some light on these problems.

REVIEW OF LITERATURE

From a review of the literature it appears that little chemical work has been done on the composition of nodules and of inoculated and uninoculated plants. Stoklasa (12) analyzed the roots, nodules and tops of soybean plants at various stages of growth and found the nodules richest in nitrogen at the blooming period. The percentage of nitrogen after the blooming period gradually decreased until at maturity the nodules contained little more nitrogen than the roots. Stoklasa (12) determined percentages of proteins, "amides" and asparagin in nodules. The protein was determined by Stutzer's reagent, the amides by nitrogen in the filtrate from Stutzer's reagent and from phosphotungstic acid and the asparagin by the ammonia distilled from magnesium oxide in the same filtrate. The results of these analyses, giving the percentage of nitrogenous compounds in dry matter of lupine nodules, follow:

STAGE OF GROWTH	PROTEIN	AMIDE	ASPARAGIN
	per cent	*per cent*	*per cent*
Blossom	3.99	0.39	0.34
Fruit	1.54	0.15	Trace

[1] Part III of thesis submitted to the faculty of the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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This opportunity is taken to express to Professors Fred and Hart, due appreciation for their suggestions and criticisms.

Stoklasa was unable to identify ammonia in the nodules. He found a trace of nitrate nitrogen at flowering stage but this disappeared at fruiting. He showed further that when flowering plants were kept in darkness for 13 days there was an increase in asparagin but a decrease in dry matter, protein, lecithin, hexose and oxalic acid in the nodules as well as in the leaves. From these results he concludes that the constituents of the leaves and nodules were the same, and that nitrogen was obtained through the leaves and there formed "amides," and that these "amides" migrated to the nodules and there reacted with glucose to form protein.

Smith and Robinson (11) found a large increase in crude protein in inoculated as compared with uninoculated seeds, leaves and stems of soybean plants, but somewhat less nitrogen in the roots. They reported that the difference in the leaves was "true" protein, but in the stems the difference was due to "amide" nitrogen. The excess nitrogen from uninoculated roots also was due to "amides."

Whiting (16) studied the composition of inoculated tops, roots and nodules of soybeans grown in nitrogen-free sand at various stages of growth. He reported total nitrogen, water-soluble nitrogen, and nitrogen precipitated by phosphotungstic acid at various stages of growth. Sana (10) showed that bacteroidal tissue of nodules from *Vicia Faba* contained 0.935 per cent of nitrogen while the cortical layer contained only traces. The age or stage of growth when these analyses were made is not given. He identified l-asparagin and leucin from the soluble nitrogenous constituents of nodules.

Several compounds have been suggested as the first assimilation product by nitrogen-fixing bacteria but practically no experimental data have been offered in support of any of them. The compounds have been suggested largely on the basis of the assumption of an analogy between fixation by bacteria and fixation by artificial methods. Gautier and Drouin (1) propose that nitrogen of the air is first oxidized to nitrous and then to nitric acid. Loew and Aso (6) believed that ammonium nitrite is the first compound formed. They state their belief as based on the assumption that the decomposition of ammonium nitrite into nitrogen and water is a reversible reaction. They state ammonia has not been found in nodules but that nitrites are sometimes found. Hutchinson and Miller (5) reported a considerable quantity of ammonia from nodules, but the reliability of the method employed is questionable. They determined ammonia by distilling the nodule extract from magnesia under reduced pressure. Hart and Bentley (3) showed that the amide nitrogen in asparagin is split off quantitatively by distilling from magnesia at 100°C. Since the work of Stoklasa (12) and Sana (10) as well as data presented in this paper indicate that nodules are rich in asparagin, confirmation of the presence of ammonia by some other method is necessary before drawing any definite conclusions.

Heinze (4) found hydrocarbons of the acetylene series in impure cultures of *Azotobacter* but was unable to identify them in pure culture. He believed

nitrogen first united with some compound in a manner similar to the formation of hydrocyanic acid from acetylene and nitrogen. Gerlach and Vogel (2) refuted the theory of Beijerenck and Van Deusen that a soluble nitrogen compound was first formed by *Azotobacter* by showing that soluble nitrogen was not present in cultures after fixation had taken place. Their view was similar to Heinze's. These workers called attention to the large energy requirement of bacteriological as well as artificial fixation. One thousand milligrams of glucose are required to fix 9 mgm. of nitrogen. Winogradsky (17) believed that nitrogen unites with nascent hydrogen of the cells to form ammonia.

As already stated these theories are supported by no satisfactory data. Whiting (16) pointed out that neither nitrite, nitrate, nor ammonia have ever been found in nodules or in plants grown in nitrogen-free media.

EXPERIMENTAL

Are cyanides present in nodules?

It is seen from this brief review of the literature that little is known of the forms of nitrogen in the nodule. None of the workers reported an attempt to identify the cyanide radical in nodules although it was twice suggested as the first product of assimilation. By a combination of Viehoever, Johns and Alsberg (14, 15) methods, very small amounts of hydrocyanic acid (0.01 mgm.) may be detected. Accordingly, it was decided to attempt to identify the cyanide group by this method, using relatively large amounts of material. Preliminary tests upon both inoculated and uninoculated fresh green plants gave negative results. Test for the cyanide radical in nodules was made as follows:

About 100 gm. of nodules were collected from soybean plants containing half-grown beans. The nodules were immediately crushed between the fingers and placed in 95 per cent alcohol to check all vital activity. Only enough alcohol was used to keep the nodules well immersed. Nodules and alcohol were poured into a mortar as soon as the laboratory was reached and the nodules were further macerated. The mixture was then transferred to a distilling flask and sufficient water added to give a volume of 300 cc. Enough sulfuric acid was added to give a strength to the solution of 8 per cent acid. The flask was attached to a condenser and immersed in an oil bath at 175°C. and distilled. The distillate was collected in a solution containing 0.5 gm. of potassium hydroxide. The end of the condenser was immersed in the liquid. Two hundred cubic centimeters were thus collected. The distillate was then concentrated to 1 cc. at diminished pressure and a temperature less than 70°C. A small crystal of potassium fluoride was added and then 1 cc. of 2 per cent ferrous sulfate. The concentration was continued to dryness and 1 cc. of 30 per cent nitric acid was added. No blue color was obtained even on standing. This determination was repeated except that alcohol was first driven off on the water bath. The experiment was again repeated on nodules

of flowering plants (about 20 gm.) and on nodules from plants containing nearly full-grown seed (approximately 100 gm.). The results in all cases were negative.

Crude analyses; solubility of nitrogen

Sixty grams of air-dry nodules were collected from the "Hill Farm" of the University in addition to those used for the cyanide determinations. A crude complete analysis gave the following results:

	per cent
Protein (N × 6.25)	27.40
Fat	1.19
Fiber	7.49
Nitrogen-free extract	51.52
Ash	6.02

Some comparative studies were made between soybeans and nodules with special reference to the solubility of nitrogen in the latter, the results of which are given in table 1. Each solubility determination was made on the original material.

TABLE 1

Comparative analyses of soybean seeds and nodules from fertile soil

	SOYBEAN SEEDS		NODULES	
	Basis of dry matter	Basis of total N	Basis of dry matter	Basis of total N
	per cent	*per cent*	*per cent*	*per cent*
Total N	6.20	–	4.37	–
Total N after extracted with ether	7.53	–	4.33	–
H_2O-soluble	+	+	1.25	28.60
N soluble in 10 per cent NaCl	4.09	54.50	1.50	34.10
N soluble in 70 per cent C_2H_5OH	+	+	0.32	7.00
N soluble in 0.3 per cent NaOH	+	+	1.58	36.00
Phosphorus	0.51	8.18*	0.26	6.50*

* Ratio P to N when N = 100.
\+ not determined.

The results show that a larger percentage of the total nitrogen in soybeans is soluble in salt solution than in the case of these nodules. While the latter solution is more efficient than water as a solvent of nitrogen in nodules it is interesting to note that dilute sodium hydroxide extracts substantially the same amount as the salt solution. Nodules obtained from fruiting plants, but in a light, sandy soil poor in nitrogen, contained 5.00 per cent of nitrogen, about 40 per cent of which was soluble in water, while approximately 54 per cent was soluble in 10 per cent salt solution.

Soluble protein and proteose

Osborne and Campbell (8) have shown that most of the nitrogen in soybean seed is in the form of globulin (glycinin). As shown above a large per cent of the nitrogen in nodules is soluble in sodium chloride solution. It would, therefore, be very interesting to know whether or not the globulin of nodules, if present, is identical with that found in the seed, or whether the plant is obliged to resynthesize it before storage in the seed.

An attempt was made to isolate sufficient purified protein (especially globulin) from nodules for analysis by the Van Slyke method, and thus to compare its constitution with that of glycinin, the globulin of the soybean. The method followed was essentially that given by Osborne (17). Glycinin was first isolated from the Ito San soybean. Good yields were obtained. Dr. E. B. Fred supplied 160 gm. of air-dry nodules from Ito San soybean plants grown in an infertile sand near Princeton, Wisconsin. The nodules were collected when the plants were in fruiting stage, dried in a 37°C. incubator and were then ground in a ball mill. They contained 5.00 per cent of N when air-dry.

Eighty grams of finely ground air-dry nodules were treated with 800 cc. of 10 per cent salt solution at 40°C. and squeezed through canvas. To the brown solution sufficient baryta water was added to make the solution neutral to litmus. The solution was next centrifuged repeatedly until no more suspended matter came down. The residue obtained from the first centrifuging was treated with an additional 100 cc. of 10 per cent sodium chloride. This was also centrifuged until clear.

An analysis of the two clear solutions showed they contained 2.30 gm. of N = 2.73 per cent nitrogen from nodules, or 54.6 per cent of the total nitrogen was thus obtained. The centrifuged sodium-chloride extract was then dialyzed for 4 days in cold running water. This experiment was carried out in December and January and, therefore, no bacterial action interfered. Toluol was added as a precautionary measure. No precipitate was obtained. It was found that the equivalent of 0.70 per cent nitrogen (on the basis of 80 gm. of nodules) remained. The clear brownish solution was saturated with ammonium sulfate, filtered and washed, first with alcohol, then with ether. After washing with ether the material was filtered and air-dried. This was dissolved in water and the ammonium sulfate remaining with the precipitate and then dialyzed for 4 days. Practically all the precipitate dissolved readily.

This centrifuged liquid was further tested for globulin by treating a portion with sufficient sodium chloride to give a 0.5 per cent salt solution and passing in carbon dioxide for some time. No precipitate was obtained. Apparently, the nodules contained no protein soluble in salt solution but insoluble in water. Another portion was tested by heating on the water bath at different temperatures. No change occurred until a temperature of 85°C. was attained when a precipitate appeared. Complete precipitation took place when the solution

was at a temperature of 85 to 92°C. Prolonged boiling of the filtrate from the coagulum failed to produce even a cloudiness in the solution. The bulky precipitate was washed with water, both by decantation and on the filter. It was next washed with absolute alcohol and then with ether and dried. The dark-colored precipitate weighed only 0.4 gm.

The light red, perfectly transparent, liquid was dialyzed in two times its volume of alcohol overnight, fresh alcohol was added and the liquid again dialyzed overnight. The gelatinous precipitate thus obtained was washed first with absolute alcohol, next with ether and then dried. A light brown precipitate containing 0.036 gm. of nitrogen was obtained. The small yields showed it was impossible to obtain enough protein for study. The results show that nearly all the salt-soluble and water-soluble nitrogen was non-protein in character. There was apparently no globulin, and only a small amount of albumin and proteose.

Qualitative tests on nodule extract

The neutral aqueous extract of nodules that had been freed from suspended matter by centrifuging, and from proteins by heating, was subjected to several qualitative tests with the following results:

TEST	RESULT
Biuret	+
Hopkins-Cole	−
Bromine	−
Xantho-proteic	+
Millon's	+
Alkaline silver nitrate	+
Fehling's	+

In view of the fact that it was impossible to secure sufficient protein for analysis it was decided to subject a hydrolyzed aqueous solution of nodules previously freed from proteins to a Van Slyke analysis and to compare these results with an analysis of glycinin. It was found, however, that such a large percentage of the nitrogen in nodule extract was lost as humin that such a comparison was meaningless.

Non-protein nitrogen

Since a large amount of plants and nodules from Princeton were available, careful analyses were made of the leaves, stalks, roots, and nodules, large amounts of tissue and the same amounts of soluble nitrogen being used in all cases. The results are given in table 2. The high percentage of nitrogen precipitated by phosphotungstic acid in the nodules is notable. This was true of all the analyses made of nodules. It is interesting to note in this con-

nection that *bacteroids* which occur in the nodules of several legumes are produced outside the plant by means of certain plant bases, notably caffeine.

It is noted further that roots and leaves were both higher in basic nitrogen than the stalks. This may indicate that the basic nitrogen in the roots was influenced by the bases of the nodules. McCool and Millar showed that the sap of the roots more nearly reflected the concentration of the soil solution than did the sap of the tops. It is, therefore, possible that the composition of the nodules influences the composition of the roots more than the tops. A careful study of the basic nitrogen of the roots of plants receiving their nitrogen from nodules as compared with those receiving their nitrogen from different planes of nitrate may throw some light on this problem. Since large amounts of tissue would be necessary it would be advisable to grow the tissue in nitrogen-poor soil in the field rather than in the greenhouse. Some studies were made along this line, but the small amount of tissue available made the results inconclusive.

TABLE 2

Distribution of nitrogen inoculated soybean plants

(Expressed as per cent of water-soluble N)

	AMINO N	AMIDE N	BASIC N
	per cent	*per cent*	*per cent*
Leaves	27.8	17.2	27.7
Stalks	20.9	21.4	11.5
Roots	16.7	21.4	19.2
Nodules	16.3	19.3	62.2

Extensive comparative studies were made of the amino-nitrogen and amide-nitrogen content of inoculated and uninoculated plants. No light on the problem at hand could be obtained because the amounts of these forms present in the plant appear to depend more upon the quantity than the quality of nitrogen supplied. This was in accord with Suzuki's (13) studies on the effect of inorganic nitrogen on the accumulation of asparagin in plants.

SUMMARY

1. The first product of nitrogen assimilation by legume bacteria and the form or forms of nitrogen assimilated by the plant from the nodule are unknown.

2. Twenty to one hundred grams of soybean nodules collected in the field at the flowering and during the fruiting of the plant do not contain the cyanide radical according to a method delicate to 0.01 mgm. of hydrocyanic acid.

3. The amount and solubility of nitrogen in nodules from different varieties of soybeans obtained from different fields, fertile and infertile, and in different years, but collected at about the same stage of growth, were somewhat different. Thirty to forty per cent of the total nitrogen in nodules was soluble in water, while from 40 to 55 per cent of the nitrogen was soluble in 10 per cent salt solutions, or in dilute alkali. The solubility in the latter solvents was nearly the same.

4. A study of the kinds and amounts of soluble protein in nodules showed that they contained apparently no globulin, and only a small amount of albumin. About 3 per cent of the water-soluble nitrogen was in the form of protein and proteose.

5. Of the protein-free soluble nitrogen in the nodules about 16 per cent of the total water-soluble nitrogen was present as primary amino nitrogen and 19.3 per cent was amide nitrogen. Over 60 per cent of the total water-soluble nitrogen was precipitated by phosphotungstic acid. The amount of the latter form, based upon the percentage of total soluble nitrogen, was much larger in the nodules than in roots, tops or leaves.

6. An increase in the supply of nitrogen, either from nitrates or nodules, caused an increase in amino and amide nitrogen in the plant, but this increase was independent of the form of nitrogen supplied.

REFERENCES

(1) GAUTIER, A., AND DROUIN, R. 1892 Sur la fixation de l'azota atmospherique par le sol et les vegetaux. *In* Bul. Soc. Chim., ser. 3, t. 7, p. 84–87.

(2) GERLACH AND VOGEL 1902 Weitere versuche mit stickstoffbindenen Bakterien. *In* Centbl. Bakt. [etc.], Abt. 2, Bd. 9, p. 881–895.

(3) HART, E. B., AND BENTLEY, W. H. 1915 The character of the water-soluble nitrogen of some common feeding-stuffs. *In* Jour. Biol. Chem., v. 22, p. 477–483.

(4) HEINZE, B. 1906 Ueber Stickstoff Assimilation durch Wiedere Organismen. *In* Landw. Jahrb.. Bd. 35, p. 907.

(5) HUTCHINSON, H. B., AND MILLER, N. H. J. 1911 The direct assimilation of inorganic and organic forms of nitrogen by higher plants. *In* Centbl. Bakt. [etc.] Abt. 2, Bd. 30, p. 513–547.

(6) LOEW, O., AND ASO, K. 1908 On change of the availability of nitrogen in soils: II. *In* Bul. Col. Agr., Tokyo Imp. Univ., v. 7, p. 567–574.

(7) OSBORNE, T. B. 1912 The Vegetable Proteins, p. 13–18. Longmans, Green & Co., New York.

(8) OSBORNE, T. B., AND CAMPBELL, G. F. 1898 Proteids of the soybean. *In* Jour. Amer. Chem. Soc., v. 20, p. 419–428.

(9) OSBORNE, T. B., AND CLAPP, S. H. 1907 Hydrolysis of glycinin from the soybean. *In* Amer. Jour. Physiol., v. 19, p. 468–474.

(10) SANA, G. 1910 Chemico-physiological investigations on the tubercles of *Vicia Faba*. *In* Atti R. Accad. Lincei, Rend. Cl. Sci. Fis., Mat. e Nat., v. 19, p. 207–211. *Abs. in* Jour. Chem. Soc. [London], v. 98, pt. II, p. 993.

(11) SMITH, C. D., AND ROBISON, F. W. 1905 Observations on the influence of nodules on roots upon the composition of soybeans and cowpeas. Mich. Agr. Exp. Sta. Bul. 224.

(12) STOKLASA, J. 1895 Studien ueber die Assimilation auf Elem. Stickstoff durch Pflanzen. *In* Landw. Jahrb., Bd. 24, p. 827–863.

(13) SUZUKI, U. 1894–97 On the formation of asparagin in plants under different conditions. *In* Bul. Col. Agr., Tokyo Imp. Univ., v. 2, p. 409–457.

(14) VIEHOEVER, A., AND JOHNS, C. O. 1915 On the determination of small quantities of hydrocyanic acid. *In* Jour. Amer. Chem. Soc., v. 37, p. 601–607.

(15) VIEHOEVER, A., JOHNS, C. O., AND ALSBERG, C. L. 1916 Cyanogenesis in plants—Studies on *Tridens Flavus*. *In* Jour. Biol. Chem., v. 25, p. 141–150.

(16) WHITING, A. L. 1915 A biochemical study of certain legumes. Ill. Agr. Exp. Sta. Bul. 179.

(17) WINOGRADSKY, S. 1901 Reference in article by Jacobitz on "Assimilation des Freien Stickstoffes." *In* Centbl. Bakt. [etc.], Abt. 2, v. 7, p. 842. (Original not seen.)

THE CONCENTRATION OF THE SOIL SOLUTION AROUND THE SOIL PARTICLES

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Received for publication December 17, 1920

INTRODUCTION

On account of the supposed adsorptive property of soils it appears to be generally believed that the solution in immediate contact with the surface of the soil particles has a greater concentration, or density, than the remainder of the solution. It is further believed that the nutritive salts in this concentrated layer are very available to plants and since the root hairs come in intimate contact with it they obtain these nutritive salts very readily.

This belief, however, of the greater concentration of the solution around the soil particles than of the mass of the soil solution has never been proved. It is deduced largely from the general principles of adsorption and from the ability of soils to take up dissolved solids.

It is the object of this paper to present experimental data and other evidences which tend to show diametrically the opposite view, namely, that the concentration of the solution around the soil particles and in the very fine capillary spaces is less concentrated than the remainder of the soil solution. These experimental data would tend also to throw some light on the question as to whether or not there really is a physical adsorption of dissolved solids by soils.

DIFFERENCE IN CONCENTRATION BETWEEN CAPILLARY-ADSORBED WATER AND FREE WATER

The evidences which go to show that the concentration of the soil solution (capillary-adsorbed water) in intimate contact with the surface of the soil particles is less than that of the mass of the soil solution (free water) may be grouped and presented under four headings: (1) The diminution of the freezing-point lowerings of soils by successive freezing and thawing; (2) the liberation of unfree water from soils by successive freezing and thawing; (3) the abnormally greater increase in the freezing-point depression of soils as the moisture content decreases; and (4) the equality in the freezing-point lowering between the supernatant liquid and the soil which it bathes.

1. The diminution of the freezing-point lowering of soils by successive freezing and thawing

It has been abundantly shown that the freezing-point method (3) is capable of measuring the concentration of the soil solution directly in the soil from any maximum to a very low moisture content, very readily and most accurately. It has been discovered by means of this method that the initial freezing-point lowering of soils tends to decrease with successive freezing and thawing. This is true with all soils, except the sands and the extreme coarse sandy loams, and from a very low to a comparatively high moisture content. The greatest diminution occurs, as a rule, in the second freezing, and gradually decreases in the succeeding freezings until the lowering of the freezing point becomes constant. Typical examples of these general results are shown in table 1.

TABLE 1

Effect of freezing and thawing on the freezing-point lowering of soils

SANDY LOAM			SILT LOAM		
Percentage of moisture	Number of times frozen	Lowering of the freezing point	Percentage of Moisture	Number of times frozen	Lowering of the freezing point
		°C.			°C.
3.9	1	0.430	16.4	1	0.430
	2	0.395		2	0.280
	3	0.390		3	0.220
	4	0.390		4	0.210
CLAY LOAM			CLAY		
15.6	1	0.820	18.3	1	0.870
	2	0.530		2	0.600
	3	0.520		3	0.470
	4	0.520		4	0.400

It is readily seen that the diminution of the initial depression of the freezing point decreased considerably by successive freezing and thawing. The diminution varies from 0.040°C. in the case of the sandy loam to 0.410° in the case of the clay.

The question now is what causes this diminution of the freezing-point depression with repeated freezing and thawing. Three hypotheses may be presented to explain this phenomenon:

1. The soils have the ability to cause a certain amount of water to become unfree. This unfree water may be in the soil either as capillary-adsorbed or chemically combined or both. In either event this unfree water is not free or active to function as a solvent but is removed from the active liquid phase and also from the field of action as far as the freezing-point lowering is concerned.

2. This unfree or inactive water is either entirely free of dissolved solids or contains only a small amount of them. At any rate, it is less concentrated than the solution which freezes at the first time.

3. The water which the soils cause to become unfree or inactive is due to the colloids which the soils contain and to the capillaries of the soils. A portion of this unfree water exists in the colloids as physically adsorbed and loosely chemically combined, and another portion as inactive capillary water in the capillaries of the soil. Upon freezing the colloids are coagulated, the bonds uniting them with the water break and some of the unfree water becomes liberated. The capillaries of the soil also are destroyed, or in some way affected by the process of freezing, and the inactive capillary water also becomes liberated. This liberated, free and dilute water from both sources goes to dilute the original soil solution and thereby decreases the lowering of the freezing point, just as the actual results show.

These hypotheses, therefore, would tend to explain the foregoing phenomenon, perfectly, and happily they appear to be correct, as will be seen in the next section.

2. The liberation of unfree water from soils by successive freezing and thawing

In order to prove whether or not soils do actually cause water to become unfree and thus refuse to freeze, the dilatometer method (1, 2) was resorted to. The principle of this method is based upon the fact that water expands upon freezing. Knowing the coefficient of expansion of the water upon freezing and also the total water content of the soil then it can easily be discovered whether all or part of the soil water freezes.

It was shown by this method that part of the water in the soil freezes very readily at a temperature slightly below 0°C., another portion does not freeze until a temperature of −78°C. is reached and a third portion does not freeze at all. These results led to the following new classification of the soil moisture.

Gravitational
Free
Unfree { Capillary-adsorbed
Combined { water of solid solution
water of hydration

Free water is that which freezes for the first time at the temperature −1.5°C. capillary-adsorbed water is that which freezes finally between −1.5° and −78°C., minus the free water and the combined water is that which does not freeze at all.

The total amount of unfree water, or that which refuses to freeze for the first time at the temperature of −1.5°, is surprisingly large, especially in the fine-textured or colloidal soils. Thus, in Superior clay it is 22.84 per cent, in Chino silty clay loam 22.52 per cent, and in Houston clay 18.03 per cent, based on the oven-dry soil, or 84.80, 85 and 63 per cent, respectively, based on the water added, which was 5 cc. to 20 gm. of soil.

The dilatometer method also showed that the process of repeated freezing and thawing actually does liberate some of the unfree water, as more of it freezes. This fact is very convincingly shown in table 2. The soils represented in this table are exactly the same as those in table 1. The same soils were used for the data in table 2 purposely to prove that the diminution of their freezing-point lowering with succeeding freezing and thawing is due to the liberation of some of their unfree water.

It is readily seen, therefore, that the amount of water which failed to freeze in the first freezing decreased with repeated freezing and thawing, proving that some of the unfree water became free and froze. The quantity of this liberated water is considerable, amounting to 4.50 per cent in the case of the silt loam.

TABLE 2

Effect of repeated freezing and thawing on the amount of water that fails to freeze in soils

SOILS AND TREATMENT	NUMBER OF TIMES FROZEN	PROPORTION OF WATER FAILED TO FREEZE; BASED ON AIR-DRY SOIL
		per cent
Sandy loam 20 gm. + 1 cc	1	1.20
	2	0.90
	3	0.90
Silt loam, 20 gm. + 3 cc	1	10.75
	2	.00
	3	6.25
	4	6.25
Clay loam, 20 gm. + 2.5 cc	1	8.75
	2	6.50
	3	6.25
	4	6.25
Clay, 20 gm. + 3 cc	1	13.25
	2	10.20
	3	9.80
	4	9.80

The diminution of the freezing-point lowering of the soil, therefore, is logically explained by the liberation of some of its water which it caused to become unfree and thus removed from the active liquid phase and also from the field of action as far as the freezing-point lowering is concerned. Since the depression in this case could be diminished only by dilution, then it naturally follows that this liberated water is very dilute or less concentrated than the mass of the soil solution which freezes readily. This conclusion is irresistible and self-evident. If the liberated water had a concentration equal to that of the mass of the active solution, the depression would be the same as before. If it had a higher concentration the depression would be greater than before.

Since, however, it is less, then it logically follows that the liberated water is less concentrated than the mass of the soil solution.

The next question that should be considered is the condition in which the unfree water exists in the soil and especially of that portion which becomes liberated upon freezing and thawing.

It will be recalled that on the basis of the dilatometer method that portion of the water which freezes very readily slightly below 0° was called free water. It was considered reasonable and logical to call this water free because pure water in mass freezes at 0°. Water which does not freeze at this temperature must be different from free water. Since the physical condition of the soil presupposes that some of its water must exist around and in the interstices of its particles, and that this water probably has a lower vapor pressure corresponding to a lower freezing point, it appeared reasonable and logical to call this water capillary-adsorbed. On the other hand, water which does not freeze at all, even at the extreme low temperature of −78°C. must also be different from the capillary-adsorbed. Since it is known that certain solid materials contain water of hydration, solid solution of water, etc., it seemed reasonable to call this water combined.

This classification, therefore, not only is supported by actual experimental results but is based upon scientific principles as well.

From the above classification and discussions it is apparent that the water which becomes liberated upon freezing and thawing must be the capillary-adsorbed. It could not very well be either the free or combined because the former is already free and freezes readily the first time, while the latter probably could not become liberated if it is in the form of water of hydration or water of solid solution. Furthermore, this combined water seems to be constant in quantity in any one soil.

That the water which becomes free upon freezing and thawing is capillary-adsorbed, seems to be beyond any doubt. As will be shown in a later paper, when a moist soil freezes the water in the larger capillaries has the power to draw to itself the water from the smaller capillaries and the films from around the particles. The water in the larger capillaries, therefore, grows at the expense of the water from the smaller capillaries and of the films. Probably the greatest portion, if not all of the water which becomes liberated and freezes in the successive freezings and thawing, is due to this fact.

Of the three different forms of water the combined exists in the most intimate contact with the soil particles, then comes the capillary-adsorbed and finally the free. Even this capillary-adsorbed water, therefore, which is not in as intimate contact with the surface of the soil particles as is the combined water, has a lower concentration than the free water, or the mass of the soil solution. This would go to indicate that the radius of influence of the soil particles is probably greater than is supposed.

As will be shown in the next section the combined water also appears to be devoid of dissolved solids, or to be much less concentrated than the free water.

All the foregoing experimental results and deductions lead to one practical and inevitable conclusion, which is the main thesis of this paper, namely, the solution around the soil particles and in the very fine capillary spaces is less concentrated than the remainder of mass of the soil solution, thus contradicting the prevalent notion.

There still remain two additional sets of evidence to be presented in support of the above conclusions. This evidence forms the subject matter of the two sections following.

3. The abnormally greater increase in the freezing-point depression of soils as the moisture content decreases

If the freezing-point depression of soils is determined at various moisture contents it will be found that the depression increases at an abnormally greater rate than the moisture content decreases. Indeed the depression tends to increase in a geometrical progression as the moisture content decreases in an arithmetical progression. A typical example of these results is shown in table 3.

TABLE 3

The freezing-point lowering of a clay loam at different moisture contents

PERCENTAGE OF MOISTURE	OBSERVED LOWERING OF THE FREEZING POINT	CALCULATED LOWERING OF THE FREEZING POINT
	°C.	°C.
10.0	1.292	
12.5	0.612	0.956
15.0	0.377	0.453
17.5	0.252	0.279
20.0	0.162	0.186
22.5	0.112	0.120

If, on the other hand, the freezing-point lowering of pure coarse quartz sand is determined at various moisture contents it will be found that in this case the depression increases in an inverse ratio as the moisture content decreases. In other words, these results follow the inverse proportionality laws and are very different from those in soils. They can be expressed by the simple mathematical equation $MD = K$ where K is the resultant constant, M the percentage of moisture and D the observed depression of the freezing point. A typical example of those results is shown in table 4.

TABLE 4

Lowering of the freezing point of quartz sand at various moisture contents

PERCENTAGE OF MOISTURE	OBSERVED LOWERING OF THE FREEZING POINT	CONSTANT K
	°C.	
2	0.091	0.182
6	0.027	0.162
10	0.018	0.180
14	0.072	0.168
18	0.009	0.162

Now when water is added to a dry soil one of the first things it would do is to dissolve the salts in the soil. If the soil acted indifferently toward the water, just as the quartz sand did, the freezing-point depression would increase inversely proportionally to the water content just as in the case of the quartz sand. Again, if some of the added water, together with its aliquot part of the dissolved salts, was caused to become unfree and thus removed from the field of action as far as the freezing-point lowering is concerned, the remainder of the soil solution should give results like those of the quartz sand. Since the actual results, however, show that the concentration of the free solution increases at a greater rate than the moisture content decreases, the inference is irresistible and logical that the soil exerts a selective action, causing only the water to become unfree and leaving behind all or most of its dissolved salts.

It would appear that the validity of this conclusion could be further proven by adding to the soil a salt solution the freezing-point depression of which was known, and if the soil abstracted from the solution only the solvent, and the solute was left behind, then the freezing-point depression of the resultant solution should be greater than the original. Unquestionably such would be the result if some salt could be found which did not react with the soil but remained inactive or indifferent. However, the soil does react to some degree with all common chemical compounds and the resultant compounds formed have a different freezing-point depression from that of the solution added. On the other hand, pure quartz flour which probably does not react with salts does give the anticipated result, namely, the concentration of the salt solution becomes appreciably greater when it is added to the quartz flour. Thus, for instance, the freezing-point lowering of KCl solution is increased from 0.390° to 0.490°C., or a difference of 0.100°, when it is added to pure washed quartz flour. This is true, however, only at very low moisture contents.

Another most interesting and significant phenomenon that should also be mentioned is the fact that the concentration of the capillary-adsorbed water in soils is less than that of the free water even when a salt solution is added to the soil and the salt reacts with the soil. It will be found that if salt solutions such as $Ca(NO_3)_2$, etc. are added to the soils and the latter are subjected to repeated freezing and thawing, results of practically the same type are obtained as in the case of pure water. Now when it is considered that the salt is not absorbed or fixed by the soil as a whole but only the base is taken up, and an equivalent amount of another base or bases is released by the soil; and when it is further considered that this fixation and exchange take place on the surface of the soil particles right where the capillary-adsorbed water is, then it seems strange and very significant that this layer of capillary-adsorbed water should be still less concentrated than the mass of the soil solution. Just what is the cause and mechanism by which this phenomenon is accomplished is difficult to say at present.

4. The equality in the freezing-point lowering between the supernatant solution and the soil which it bathes

If it were true that the soils had the power to condense or physically fix on the surface of their particles a layer of solution of greater density or concentration than the mass or volume of solution bathing the soil, then it would seem reasonable to expect that a soil bathed in an excess of salt solution should show a greater lowering of the freezing point than the supernatant liquid. A large number of experiments performed, however, with many different soils and various kinds of salt solutions and different periods of contact, failed to show that such is the case. Indeed the results showed in many cases that there was a difference in the depression in favor of the supernatant liquid. This difference, however, was extremely slight, probably on account of the large volume of solution used.

All the foregoing array of evidence, therefore, agrees and points overwhelmingly to the conclusion that the solution around or in immediate contact with the surface of the soil particles is less concentrated than the mass of the solution, which is diametrically opposed to the prevalent notion.

Again, the preceding results seem to make it very doubtful whether there really is a physical adsorption of dissolved mineral solids by soils.

SUMMARY

It appears generally to be believed that on account of the adsorptive power of soils the solution around or in immediate contact with the surface of the soil particles is more concentrated than the mass of the soil solution.

In this paper, however, there is presented experimental evidence which proves diametrically the opposite view, namely, the solution around the soil particles and in the very fine capillary spaces is less concentrated than the mass of the solution. All experimental evidence obtained is overwhelmingly in favor of this conclusion.

A correct knowledge concerning this particular point is of profound and far-reaching importance, for the proper understanding of both the soil solution and its utilization by the plants.

REFERENCES

(1) Bouyoucos, G. J. 1917 Measurement of the inactive or unfree moisture in the soil by means of the dilatometer method. *In* Jour. Agr. Res., v. 8, no. 6, p. 195–217.

(2) Bouyoucos, G. J. 1917 Classification and measurement of the different forms of water in the soil by means of the dilatometer method. Mich. Agr. Exp. Sta. Tech. Bul. 36.

(3) Bouyoucos, G. J., and McCool, M. M. 1916 Further studies on the freezing-point lowering of soils. Mich. Agr. Exp. Sta. Tech. Bul. 31.

CHEMICAL EFFECT OF SALTS ON SOILS[1]

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Received for publication December 16, 1920

INTRODUCTION

The solid, liquid and gaseous phases of a soil form a chemical system and a material change in any one of these phases must inevitably affect the equilibrium of the system. As is well known, there has long been a tendency among writers on soils to treat the subject as if a condition of stable equilibrium existed in soils, while as a matter of fact chemical reactions may be readily induced, and changes are continually taking place, with the consequent shifting of the equilibrium. As shown by Stewart (23), Hoagland (10) and Burd (3), the soluble components of cropped and uncropped soils, especially the former, are subject to wide fluctuations both quantitatively and qualitatively.

It is important that we extend our knowledge regarding the changes that salts produce in soils; for not until a thorough analysis is made of the fundamental equilibria involved, can we hope to have an adequate understanding of the physiological effects of alkali salts and of fertilizers in general.

Despite the many previous investigations on this subject, much still remains to be determined. It is important to have a clearer understanding of the nature of the reactions which take place when salts are added to soils, of the constituents on which they react, and of the resulting products of the reaction and their relations to the concentration and composition of the soil solution.

The fact that large amounts of soluble salts are continually being introduced into the soils of the semi-arid region, either as constituents of the irrigation water (14) or by capillary rise from the subsoil, gives special interest to a study of the chemical reactions involved.

A large part of the previous work[2] on this subject has been done with the use of potassium and ammonium salts (8, 22, 25, 26), such as are widely used in commercial fertilizers. When neutral solutions of these salts are brought into contact with soil, it has been shown repeatedly that for every part of potassium or ammonia absorbed by the soil, there is brought into solution a

[1] Paper No. 75, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

[2] A very complete review of the literature bearing on the effects of salts on soils is given by Sullivan (24).

chemical equivalent, or approximately so, of other bases. Calcium is usually dissolved in greatest quantity, but appreciable amounts of magnesium and sodium also are usually set free.

While it is well known that soils have the power of fixing considerable amounts of potassium and ammonia, it is not so widely recognized that sodium salts also react with soils. In fact, it is frequently stated that sodium is not fixed by soils. There is abundant evidence, however, that sodium salts produce substantial chemical reactions with many soils. Especially is this true of the soils of the semi-arid region of America. It has also been frequently claimed that calcium salts replace potassium from soils, but various investigators have been unable to demonstrate this reaction. The obvious explanation of these discrepancies lies in the inherent differences in the soils that have been studied, as was pointed out by Lipman and Gericke (20).

The amount of the reactions taking place and the specific bases replaced by a given salt seem to depend mainly on the nature and amounts of the silicates[3] present and the state of subdivision of the soil. A given base. combined in certain silicates, is far more readily replaceable than in others, Lemberg (16, 17, 18, 19) has made extensive studies on the effects of salts on minerals. His results, Eichhorn's (4) and those published more recently by Sullivan (24), are of special interest in this connection. From their investigations it was shown that salt solutions containing monovalent bases readily react with certain silicates; salts of divalent bases react with others; while neither of these classes of salts reacts with still other silicates. The reactions appear to be of the nature of an exchange of bases and are usually reversible, although the reactions do not necessarily take place with equal facility in both directions. It is probable that calcium is more easily replaced from soils than the monovalent bases.

The reaction (H-ion concentration) of salt solutions may also be materially altered by soils; and conversely, the H-ion concentration of a soil extract may be materially altered by treating the soil with soluble salts. Certain soils convert neutral salt solutions into distinctly acid solutions. Other soils, which give approximately neutral or only slightly alkaline aqueous extracts, may yield distinctly alkaline extracts after treatment with neutral salt solutions, as will be more fully discussed elsewhere.

If an adequate understanding of the effects of salts on plants grown in soil cultures is to be had, the chemical reactions induced in the soil by the treatments must certainly be considered. As suggested by Headley (7), the roots of plants must come into contact with not merely a simple aqueous

[3] Many statements occur in the agricultural literature to the effect that these reactions depend on the zeolites, but so far as we are aware, the presence of true zeolites in soils has never been proven. As shown by Lemberg (18) and Sullivan (24), salts react not only with the zeolitic minerals but with various other silicates as well. For the present we prefer, therefore, to assume these reactions to be due to silicates in general.

solution of the added salt, but with a solution after equilibrium[4] has been established between the added salt and the soil. This solution will inevitably contain the soluble products of the reactions as well as any non-reacting soluble substances present in the soil previous to the treatment. Furthermore, the evidence obtained by the determination of the freezing-point depression (2, 6), the use of the dilatometer (1) and conductivity measurements (11), indicates that the total concentration of the soil solution, to say nothing of its composition, may be materially affected as a result of adsorption, whether we consider adsorption to be a physical or a chemical process.

It follows, then, that the composition of a salt solution after having come into intimate contact with a soil, may differ materially from that of the original solution. As pointed out previously by one of us (13), various writers seem to ignore this fact, or else to consider it to be inconsequential. Especially has this been true with certain investigators of the effects of alkali salts (5).

Despite the many previous investigations, differences of view still prevail concerning the relative toxicity of the different salts and the alkali tolerance of different plants. As suggested above, the addition of like amounts of a given salt to different soils has frequently been shown to produce variable effects with a given species of plant. In many of these and other investigations on alkali soils, very little if any attention has been given to the effects of the salts on the soil itself. Various phases of this question are being studied in this and other laboratories of the California Agricultural Experiment Station.

METHODS

Two distinctly different soil types were used in this study. One soil, no. 430, was obtained from the Citrus Experiment Station, Riverside, California, and is classified as Placentia light sandy loam; the other, no. 431, from La Habra, California, is a clay loam of the Ramona series. In each case a sample consisting of several hundred pounds was taken to a depth of 1 foot. After becoming air-dry each was passed through a 2-mm. screen, thoroughly mixed and stored in bins.

Portions of each were treated with solutions of different salts in the ratio of 1 part of soil to 5 parts of solution. Four hundred grams of the air-dried soil was shaken 1 hour with 2000 cc. of the solution, then filtered through Chamberland-Pasteur tubes and the filtrate analyzed. The solutions employed were accurately standardized, being made up with the purest salts obtainable, dissolved in distilled water, from which all but traces of CO_2 had been removed by aeration.

Standard methods of analysis were employed. Usually 400 cc. of the filtrate was treated with 20 to 25 cc. of aqua regia, evaporated to dryness, the

[4] We do not mean to give the impression that true equilibrium in the physico-chemical sense persists for any considerable period of time in soils.

residue taken up with dilute HCl and filtered to remove SiO_2. The resulting filtrate was analyzed for Ca, Mg, K and Na. Separate aliquots were titrated with 0.05 *N* H_2SO_4 for CO_3 and HCO_3, phenolphthalein and methyl orange being used as indicators. Chlorine was determined by titration in a separate aliquot. Nitrate was determined colorimetrically when present in small amounts and by reduction with aluminum when present in relatively large amounts. Sulfate was determined gravimetrically and phosphate volumetrically. Ammonia was determined by distillation with magnesium oxide. The pH values of the filtrates were determined colorimetrically, Clark and Lubs indicators and buffer solutions being used. The results are expressed in parts per million of the extracts.

EXTRACTS WITH WATER

In table 1 are given the analyses of water extracts of these soils. The extracts were obtained by shaking the soil with carbon dioxide-free distilled

TABLE 1

Composition of water extracts of soils

(p.p.m. of solution)

	SOIL 430	SOIL 431
Calcium (Ca)	4	6
Magnesium (Mg)	2	3
Potassium (K)	3	6
Sodium (Na)	4	4
Chlorine (Cl)	2	4
Carbonate (CO_3)	0	0
Bicarbonate (HCO_3)	12	17
Sulfate (SO_4)	4	7
Nitrate (NO_3)	1	5
Phosphate (PO_4)	3	1
Silica (SiO_2)	5	5
Total soluble solids	48	93
pH	7.0	7.1

water in the ratio of 1:5. The results, as in the case of the salt solutions, are expressed in parts per million of the extracts. If desired, the data may be readily converted into parts per million of the air-dried soil by multiplying by 5.

Each of these soils had been cropped with grain for many years without irrigation or the application of fertilizer. As the data show, the solubility of each is low, especially so in the case of soil 430. It is also of interest to note that each soil gave approximately neutral extracts. Furthermore, other studies show that neither of them contains more than traces of insoluble carbonates. No. 430 is a soil of low crop-producing power, while the yields from no. 431 are still reasonably good.

EFFECT OF NEUTRAL SALT SOLUTIONS

The effects of 0.01 *N* solutions of sodium, potassium, ammonium, calcium and magnesium chlorides are shown in tables 2 and 3; the effects of the corresponding sulfates in tables 4 and 5, and the effects of sodium and potassium nitrates in table 6.

It will be noticed that the chloride, sulfate and nitrate of a given base produced approximately the same effect on a given soil, but the amount of the reactions which took place was much greater with soil 431 than with soil

TABLE 2

Effect of chlorides on soil 430

(p.p.m. of solution)

	0.01 *N* SOLUTIONS				
	NaCl	KCl	NH_4Cl	$CaCl_2$	$MgCl_2$
Calcium (Ca)	18	41	38	175	62
Magnesium (Mg)	6	11	9	16	83
Potassium (K)	10	290	20	13	16
Sodium (Na)	210	5	2	6	8
Chlorine (Cl)	356	356	358	355	356
Ammonia (NH_4)			130		

TABLE 3

Effect of chlorides on soil 431

(p.p.m. of solution)

	0.01 *N* SOLUTIONS				
	NaCl	KCl	NH_4Cl	$CaCl_2$	$MgCl_2$
Calcium (Ca)	45	84	80	153	134
Magnesium (Mg)	12	21	19	29	45
Potassium (K)	18	178	34	19	23
Sodium (Na)	174	7	5	14	10
Chlorine (Cl)	360	360	360	359	360
Ammonia (NH_4)			72		

430. In general, it may be said that the differences noted in these two soils are quantitative rather than qualitative. Soil 431 contains considerably more of the finer fractions than no. 430. The amount of surface exposed to the solutions was, therefore, probably considerably greater with the former than with the latter.

If we take into consideration the water-soluble constituents of these soils, it is apparent that the anion of none of the neutral solutions was materially changed by the soil. The cation content, on the other hand, was substantially modified. It appears that the reactions are largely in the nature of an exchange of bases. Simple calculation shows that for every part of base

absorbed from solution, an approximately equivalent amount of other bases passed into solution. In fact, this must be true, since neither the reaction (H-ion concentration) nor the anion content of the solutions was appreciably affected by the soil.

TABLE 4

Effect of sulfates on soil 430

(p.p.m. of solution)

	0.01 *N* SOLUTIONS				
	Na_2SO_4	K_2SO_4	$(NH_4)_2SO_4$	$CaSO_4$	$MgSO_4$
Calcium (Ca)	18	48	40	177	62
Magnesium (Mg)	8	12	9	15	84
Potassium (K)	21	278	18	14	15
Sodium (Na)	195	4	2	2	5
Sulfate (SO_4)	484	470	476	478	474
Ammonia (NH_4)			121		

TABLE 5

Effect of sulfates on soil 431

(p.p.m. of solution)

	0.01 *N* SOLUTIONS				
	Na_2SO_4	K_2SO_4	$(NH_4)_2SO_4$	$CaSO_4$	$MgSO_4$
Calcium (Ca)	45	93	83	153	112
Magnesium (Mg)	11	23	20	29	49
Potassium (K)	27	183	29	21	22
Sodium (Na)	155	6	5	4	4
Sulfate (SO_4)	498	483	483	474	475
Ammonia (NH_4)			66		

TABLE 6

Effect of nitrates on soils

(p.p.m. of solution)

	SOIL 430		SOIL 431	
	0.01 *N* solutions		0.01 *N* solutions	
	$NaNO_3$	KNO_3	$NaNO_3$	KNO_3
Calcium (Ca)	17	44	45	89
Magnesium (Mg)	6	11	13	23
Potassium (K)	27	297	29	162
Sodium (Na)	198	4	164	6
Nitrate (NO_3)	629	626	635	629

The amount of the reactions was least, although considerable, with sodium salts and greatest with magnesium salts. Potassium and ammonium salts produced intermediate and approximately equal effects.

Calcium is the base most readily replaced in these soils, while small increases in the solubility of potassium and magnesium also were produced by each of the salts. By comparing these data with those in table 1 it will be seen that both calcium sulfate and calcium chloride brought about increases in the solubility of the potassium and magnesium in each soil.

The effects of potassium, ammonium, calcium and magnesium salts on the solubility of sodium were variable and in no case very great. In view of the

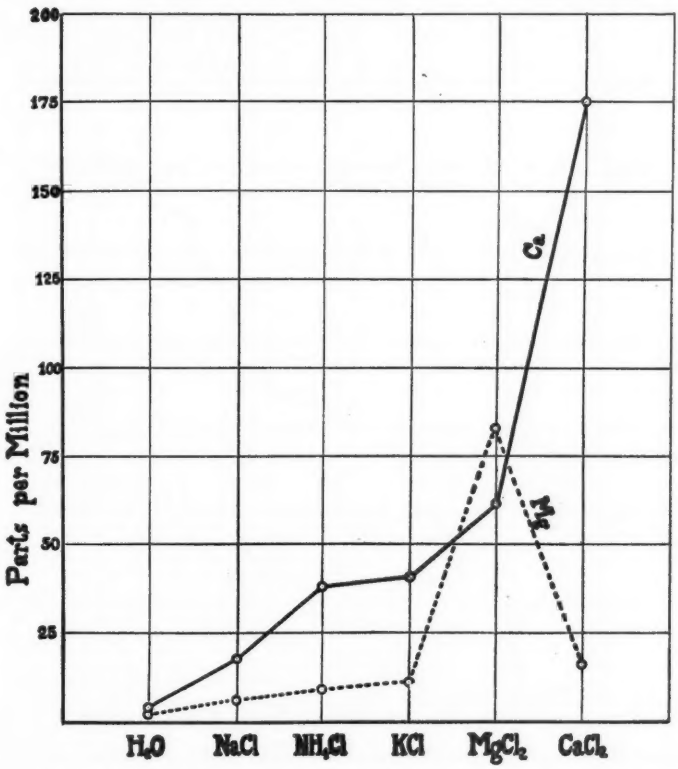

FIG. 1. GRAPHS FOR SOIL 430 SHOWING Ca AND Mg SOLUBLE IN WATER AND IN 0.01*N* SOLUTIONS OF VARIOUS CHLORIDES

magnitude of the analytical error involved in the determination of sodium, it is doubtful whether any significance should be given these variations.

The effects of the different salts are especially striking in the case of soil 431. Sodium, potassium, ammonium and magnesium salts all replaced substantial amounts of calcium from this soil. With the use of ammonium salts the extracts were found to contain greater amounts of calcium than of ammonia remaining in solution, while with the use of magnesium salts the

extracts contained more than twice as much calcium as magnesium. The results were similar, but less striking, with soil 430. The effects are well illustrated by the curves (fig. 1, 2, 3 and 4).

The H-ion concentration of most of the solutions was determined, both before and after shaking with the soil, by the use of standard buffer solutions, but as stated above, very little if any change took place.

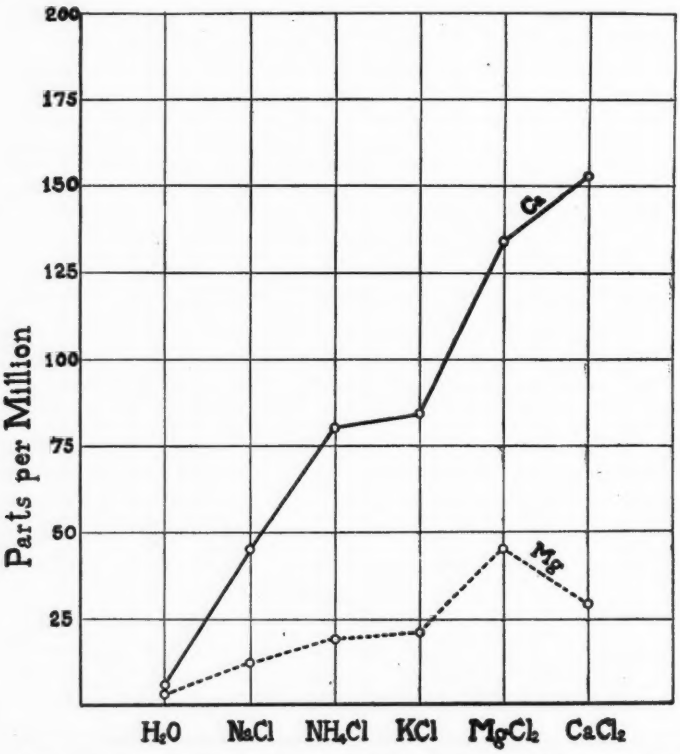

FIG. 2. GRAPHS FOR SOIL 431 SHOWING Ca AND Mg SOLUBLE IN WATER AND IN 0.01*N* SOLUTIONS OF VARIOUS CHLORIDES

These data are of interest as bearing on studies on the effects of salts on plants. In the case of soil 431 it is evident that, following the addition of any of these sodium salts, the soil moisture will contain substantial increases in the amounts of calcium in solution. As shown by Kearney and Cameron (12), Le Clerc and Breazeale (15) and others, the physiological effects of sodium chloride may be profoundly modified by the presence of calcium salts.

The data obtained by the use of magnesium salts show the extreme importance of considering the reactions induced in the soil. Kearney and

Cameron (12) have shown that while magnesium salts in simple solutions are highly toxic, the presence of soluble calcium enormously decreases the toxicity

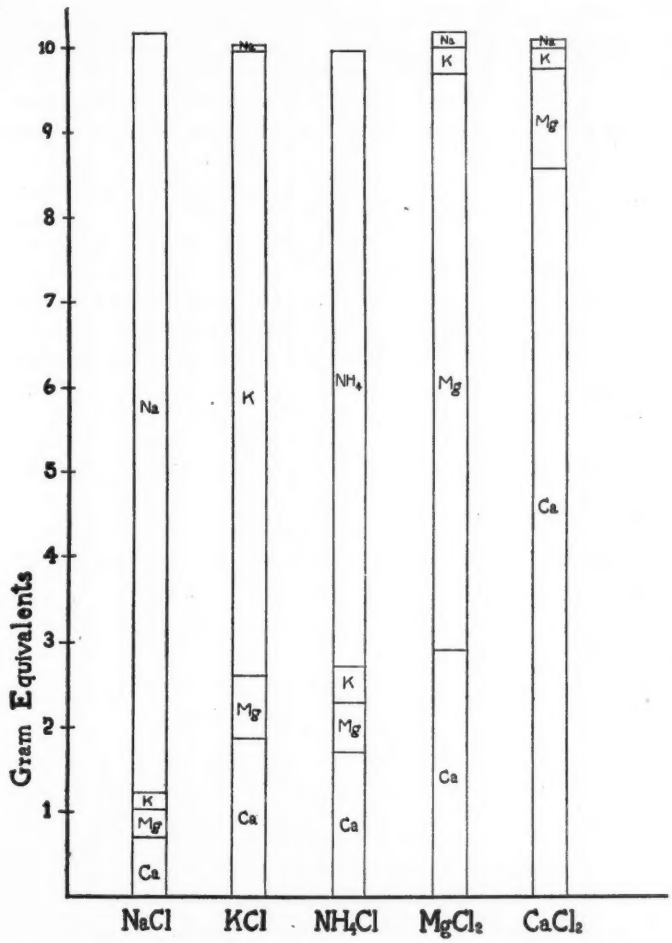

FIG. 3. GRAPHS SHOWING CATIONS FOUND IN EXTRACTS OBTAINED BY SHAKING 1 PART OF SOIL 430 WITH 5 PARTS OF 0.01*N* SOLUTIONS OF VARIOUS CHLORIDES

Calculated as gram-equivalents per 1000 liters; original solutions contained 10 gram-equivalents per 1000 liters.

of magnesium. The data show that with the use of 0.01*N* magnesium salts, plant roots in soil 431 would be in contact with a solution containing even greater molecular concentrations of calcium than of magnesium (fig. 4). In

this case, it would be more nearly correct to consider the nutrient solution as a calcium solution, than as a magnesium solution.

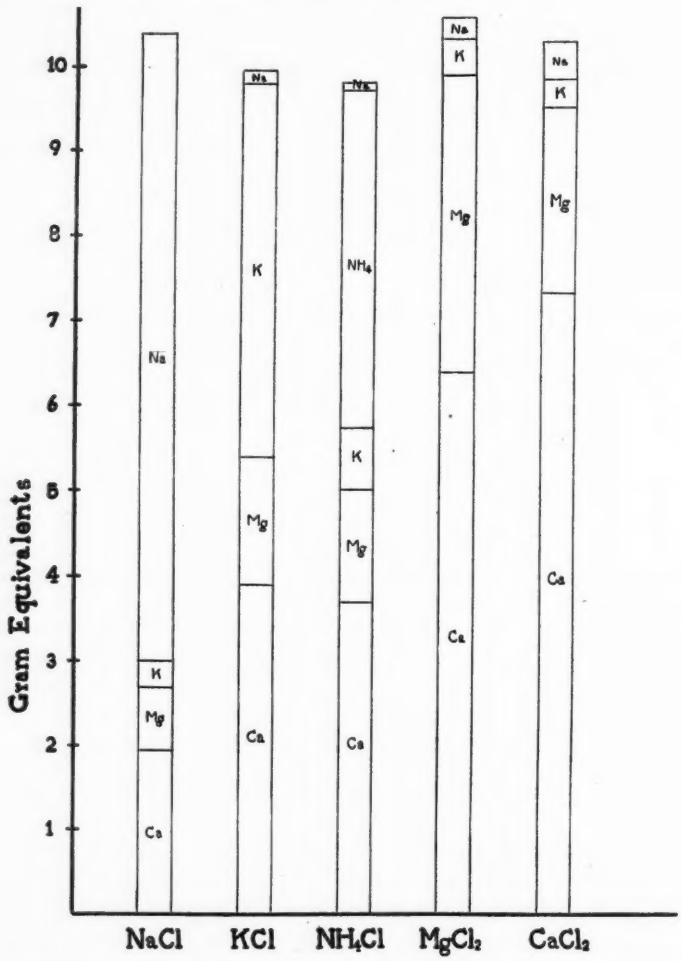

FIG. 4. GRAPHS SHOWING CATIONS FOUND IN EXTRACTS OBTAINED BY SHAKING 1 PART OF SOIL 431 WITH 5 PARTS OF 0.01*N* SOLUTIONS OF VARIOUS CHLORIDES

Calculated as gram-equivalents per 1000 liters; original solutions contained 10 gram-equivalents per 1000 liters.

In the light of these data it is self-evident that different physiological effects may be expected to result from the use of the same salt on different soils. Furthermore, the effects in any ordinary soil are likely to be materially different from those in sand or water cultures.

EFFECT OF PHOSPHATES

Preliminary studies have been made on the effects of soluble phosphates. The results are recorded in table 7. Solutions of di-sodium phosphate, mono-sodium phosphate and mono-calcium phosphate were employed, the strength of each solution being 0.01 *N* with respect to PO_4. Since PO_4 is trivalent, the sodium content of the first and second of these solutions was only two-thirds and one-third, respectively, of that of the neutral sodium salts previously discussed. The solutions of mono-sodium phosphate and mono-calcium phosphate were, of course, distinctly acid. With these latter salts the chemical reactions which took place were probably of a more complex nature than with the neutral sodium salts.

It is interesting to note that in the case of soil 430 the extracts obtained by the use of di-sodium phosphate contained no more calcium than the water extract (table 1), and those obtained with mono-sodium phosphate contained very much less calcium than the extracts obtained with the neutral sodium

TABLE 7

Effect of phosphates on soils

(p.p.m. of solution)

	SOIL 430			SOIL 431		
	0.01 *N* solutions			0.01 *N* solutions		
	Na_2HPO_4	NaH_2PO_4	$Ca(H_2PO_4)_2$	Na_2HPO_4	NaH_2PO_4	$Ca(H_2PO_4)_2$
Calcium (Ca)	4	9	54	12	17	43
Magnesium (Mg)	4	5	6	7	7	12
Potassium (K)	5	8	7	9	10	11
Sodium (Na)	133	73	8	89	57	12
Phosphate (PO_4)	304	309	291	258	275	255

salts. As will be shown later, the concentration of sodium ions in the solutions partly accounts for this difference, but precipitation of the products of the reactions as insoluble phosphates was also involved.

The original solutions contained 317 parts per million of PO_4. After contact with the soils, the di-sodium phosphate solution contained only 304 and 258 parts per million, respectively. The soil which yielded the greater amount of divalent bases to the neutral solutions (431) precipitated the greater amount of PO_4. The same is true with the mono-basic phosphate of sodium, although the acidity of this solution tended to prevent the precipitation of phosphate.

With the use of mono-calcium phosphate, substantial amounts of PO_4 were precipitated, probably largely on account of the action of the H ions in dissolving from the soil bases which then formed insoluble phosphates. In consequence of this reaction, the acidity of the solution was lowered and a partial precipitation of the calcium as insoluble phosphates resulted. From the

evidence at hand, we are inclined to believe that the well known power of soils to fix phosphate is very largely attributable to chemical reactions with the formation of insoluble phosphates. We believe, as in the case of other salts, that the fixation of phosphates by soils may be satisfactorily explained by giving due consideration to the solubility of the products of the reaction and to the principle of mass action.

EFFECT OF ALKALINE SOLUTIONS

In this experiment 0.01 *N* solutions of $NaHCO_3$, Na_2CO_3 and NaOH, and 0.1 *N* Na_2CO_3 and NaOH were used. In addition to the bases determined previously, HCO_3, CO_3, OH and SiO_2 and pH values also are reported. The results are recorded in tables 8 and 9.

TABLE 8

Effect of alkaline solutions on soil 430

(p.p.m. of solution)

	0.01 *N* SOLUTIONS			0.1 *N* SOLUTIONS	
	$NaHCO_3$	Na_2CO_3	NaOH	Na_2CO_3	NaOH
Calcium (Ca)	8	3	3	13	2
Magnesium (Mg)	3	2	5	5	8
Potassium (K)	13	13	3	7	7
Sodium (Na)	200	167	108	2156	2045
Bicarbonate (HCO_3)	573	287	0	830	0
Carbonate (CO_3)	0	87	138*	2472	52†
Hydrate (OH)	0	0	3	0	1263
Silica (SiO_3)	3	4	19	9	54
pH	8.4	9.2	9.6		

* A part of the alkalinity may have been due to sodium silicate.

† Equal to 66 p.p.m. of SiO_3.

It will be noted that the amounts of the different bases found in these extracts were widely different from those obtained by the use of neutral sodium salts. The calcium content was substantially less, particularly where sodium carbonate and sodium hydrate were used (fig. 6). The concentration of soluble magnesium also was materially less than in the neutral solutions, as was also that of potassium in the sodium-hydrate extracts. It is reasonable to infer that the same general types of exchange of bases took place with the alkaline as with the neutral salts of sodium, but that precipitation of calcium and magnesium as insoluble carbonates and silicates took place, with the result that the amounts remaining in solution were low.

It is especially interesting to note that while the sodium content of the extract obtained from a given soil by the use of sodium bicarbonate was practically equal to that obtained by the use of neutral sodium salts, the sodium was removed from solution in increasing amounts as we pass from the

less to the more highly alkaline solutions (22) (fig. 6). Each solution originally contained the same concentration of sodium. In addition to the exchange of bases, by which a portion of the sodium was removed from solution, so-

TABLE 9

Effect of alkaline solutions on soil 431

(p.p.m. of solution)

	0.01 *N* SOLUTIONS			0.1 *N* SOLUTIONS	
	$NaHCO_3$	Na_2CO_3	NaOH	Na_2CO_3	NaOH
Calcium (Ca)	26	7	6	23	5
Magnesium (Mg)	7	3	5	16	13
Potassium (K)	21	18	5	16	12
Sodium (Na)	156	116	38	1357	1278
Bicarbonate (HCO_3)	531	346	46	1360	0
Carbonate (CO_3)	0	0	10	1152	360*
Hydrate (OH)	0	0	0	0	785
Silica (SiO_2)	11	7	9	14	174
pH	8.0	8.2	8.5		

* Equal to 456 p.p.m. of SiO_3.

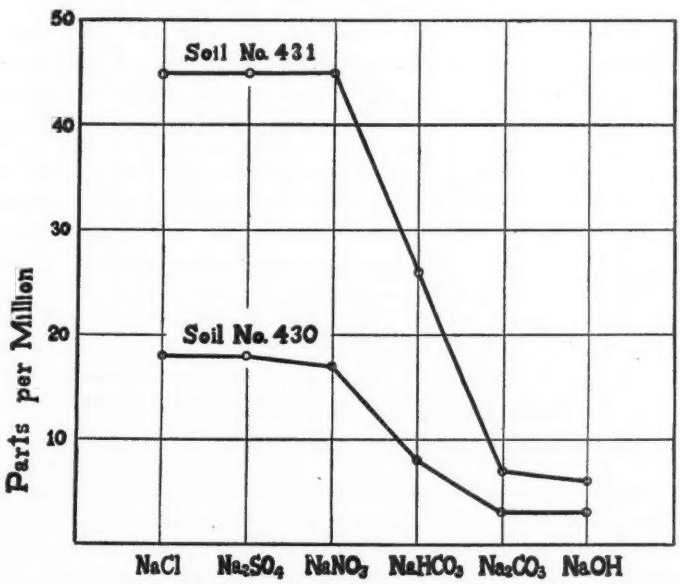

FIG. 5. GRAPHS SHOWING EFFECT OF 0.01*N* SOLUTIONS OF VARIOUS Na SALTS ON THE SOLUBILITY OF Ca IN SOILS

dium carbonate and sodium hydrate probably also reacted with colloidal silica with the resulting solution of small amounts of silica and the formation of colloidal sodium silicate.

The effects of the soil on the OH-ion concentration is especially interesting. The data show that each soil converted substantial amounts of normal carbonate into bicarbonate. With soil 431 not more than a trace of normal carbonate was left in the 0.01 *N* solution and more than half of the CO_3 in the 0.1 *N* Na_2CO_3 solution was converted into HCO_3. Soil 430 produced the same type of reaction but to a much less degree.[5] The alkalinity of the NaOH solution also was very materially lowered. In fact, soil 431 reduced the alkalinity (OH-ion concentration) of the 0.01 *N* NaOH solution to a point closely approaching that of 0.01 *N* $NaHCO_3$.

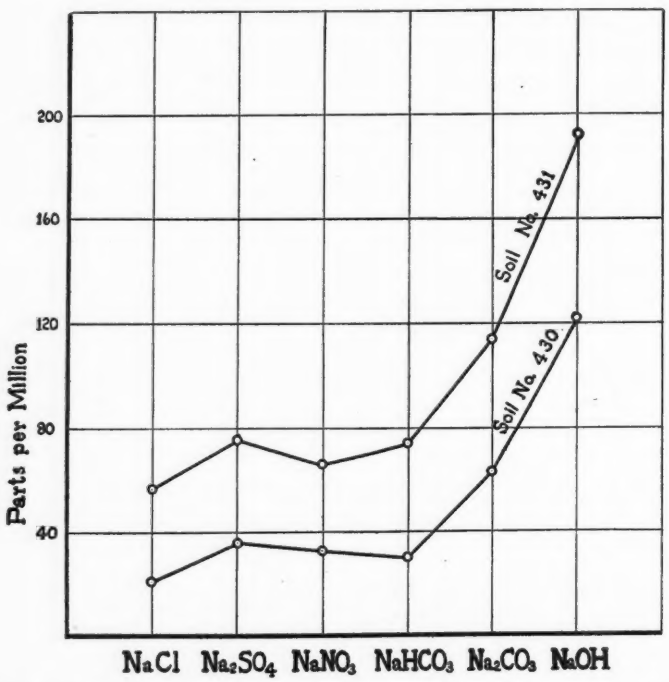

FIG. 6. GRAPHS SHOWING THE FIXATION OF Na BY SOILS (230 P.P.M. OF Na ADDED)

The effect of these soils on the OH-ion concentration of alkaline solutions is probably of a rather complex nature. Precipitation of insoluble carbonates, the solution of silica and reaction with silicic acids with the resulting evolution of CO_2, the replacement of hydrogen from complex silicates by sodium, and reactions with organic substances, all probably played a part. The facts that only very small amounts of SiO_2 were found in the 0.01 *N* Na_2CO_3

[5] It will be shown in a subsequent paper that the conversion of CO_3 into HCO_3 was not due to the action of CO_2 present in the compressed air used in filtering these solutions.

solutions and that the reaction of the extract from soil 431 had been reduced to a pH value of 8.2 and contained relatively large amounts of HCO_3, suggest that the silicates of this soil may contain replaceable hydrogen. The lowering of the alkalinity, however, may have been due to reactions with organic matter. These extracts were distinctly colored and contained considerable dissolved organic matter. Whatever may be the true explanation of these data, it is apparent that substantial chemical reactions took place.

The foregoing data show at once that in studying the effects of soluble salts on plants, the chemical reactions taking place between the solution and the soil must be considered. Even with the use of a neutral salt, NaCl for example, the roots of plants will come in contact with a mixed salt solution the composition of which may vary materially in different soils.

Where the purpose is to compare the effects of neutral and alkaline salts, the reactions may become of paramount importance, and unless cognizance be taken of this fact, totally erroneous conclusions may be drawn.

The data show that the ratios of the several bases dissolved from these soils by molecularly equivalent solutions of strongly alkaline and neutral sodium salts differed widely. The anion content of the neutral solutions was not materially changed by the soils, but relatively large amounts of Na_2CO_3 were converted into $NaHCO_3$ with the resulting reduction in alkalinity. It is evident that no reliable conclusions can be drawn regarding the comparative toxicity of NaCl or Na_2SO_4 and Na_2CO_3 unless these reactions be definitely determined, and their physiological significance be positively established.

Since the two soils studied produce these reactions in varying degrees, and there is a strong probability that other soils will likewise vary in their power to react with salts, both quantitatively and qualitatively, it is not surprising that investigators have not been able to agree concerning the alkali tolerance of plants. It seems evident that until more complete data are obtained on the chemical reactions that take place and on the phenomenon of adsorption in soils, and more comprehensive studies are made on the physilogoical significance of different ionic ratios, confusion is likely to prevail among students of the alkali problem.

In view of the various reactions which take place between salts and soils and the fact that the activity of micro-organisms produces important, yet variable changes in the soluble matter of soils,[6] it seems safe to say that water cultures must continue to be relied upon for the determination of the physiological principles underlying the effects of salts on plants. Any solid medium to be suitable for this purpose must be essentially inert towards the nutrient solution, and pure quartz sand probably affords the nearest approach to this condition.

[6] The effects of CO_2 generated by micro-organisms in addition to that given off by the roots of plants and germinating seeds, may in itself be sufficient to lower the alkalinity of a nutrient solution very materially (9).

The above data also are of interest in connection with methods for the determination of the total alkalinity in soils containing sodium carbonate. As already suggested, sodium carbonate and other sodium salts to a lesser degree seem to react with the silicates present to form compounds relatively high in sodium, yet not readily soluble in water. Such compounds, however, are probably somewhat more soluble than the corresponding calcium salts and undergo slow hydrolysis with the continued formation, for an indefinite period, of sodium hydrate. This latter combines with the ever present carbon dioxide of soils to form sodium carbonate.

It has been found that certain soils to which sodium carbonate has been added, and the same is also true of soils in which sodium carbonate occurs naturally, continue to yield highly alkaline solutions upon repeated extraction with successive portions of pure water. In the practical reclamation of black alkali soil it is probably necessary not only to reduce the concentration by leaching away the excessive amounts of soluble salts present, but in some cases at least it may be necessary also to convert the sodium silicates into calcium silicates, as will be more fully discussed in a subsequent paper.

EFFECT OF CONCENTRATION

The solutions of the neutral salts employed above were of 0.01 *N* strength. It is also a matter of interest to study the effects of other concentrations. For this purpose seven different concentrations of NaCl were used ranging from 0.001 *N* to 0.2 *N*. The results are recorded in tables 10 and 11.

It will be noted that the more concentrated solutions replaced greater amounts of calcium, magnesium and potassium than the weaker solutions. With both soils 0.1 *N* NaCl replaced fully as much magnesium as 0.2 *N* solution, whereas the 0.04 *N* solutions replaced the maximum amounts of potassium. On the other hand, the amounts of calcium set free increased progressively with the strength of the solution. The results are well illustrated by the curves in figure 7. In general the exchange of bases follows the mass-action law.

These data are of interest from the standpoint of studies on the effects of NaCl on plants. They indicate that the composition of the soluble salts in solution in the soil moisture following the addition of NaCl of varying strengths will differ, not only quantitatively, but qualitatively as well. In other words, the roots of plants under such conditions must come in contact with solutions containing varying amounts of other ions as well as of sodium. In view of the probable influence of calcium chloride on the toxicity of sodium chloride the use of different soils in such a study introduces factors, the influence of which may materially modify the physiological effects of the NaCl and lead to erroneous conclusions regarding the toxicity of NaCl itself.

Frequently the dry salt is first mixed with the soil, then water added to effect the desired moisture content. Under such conditions it is probable

that the soil solution will contain somewhat greater amounts of calcium than if the same amount of salt were added as a solution. The reaction between soluble salts and soils is extremely rapid and since it is roughly proportional to the concentration, relatively large amounts of calcium will be set free as the particles of salt dissolve, since local zones of relatively high concentration will temporarily occur.

Preliminary studies have also been made by repeatedly extracting a given portion of soil with sodium chloride solution. By this means the products of the reaction were removed from the soil. It was found that the exchange of bases can be considerably increased over that which takes place by a single treatment.

TABLE 10

Effect of different concentrations of NaCl *solutions on soil 430*

(p.p.m. of solution)

	CONCENTRATION						
	0.001 *N*	0.002 *N*	0.01 *N*	0.02 *N*	0.04 *N*	0.1 *N*	0.2 *N*
Calcium (Ca).....	5	6	18	25	39	68	111
Magnesium (Mg).....	2	3	6	7	10	14	12
Potassium (K).....	4	5	10	7	11	8	
Sodium (Na).....	22	42	210	412	854	2171	4435
Chlorine (Cl).....	36.5	70.6	356	702	1418	3528	6957

TABLE 11

Effect of different concentrations of NaCl *solutions on soil 431*

(p.p.m. of solution)

	CONCENTRATION						
	0.001 *N*	0.002 *N*	0.01 *N*	0.02 *N*	0.04 *N*	0.1 *N*	0.2 *N*
Calcium (Ca).....	10	15	45	70	114	214	333
Magnesium (Mg).....	3	4	12	17	27	41	38
Potassium (K).....	8	9	18	14	20	18	
Sodium (Na).....	15	34	174	349	752	1951	4098
Chlorine (Cl).....	39.0	73.7	360	712	1429	3553	7021

After extracting with NaCl solution the same portions of soil were shaken with $CaCl_2$ solution. The results show that the sodium previously fixed by the soil is capable of substitution by soluble calcium. In other words, the reaction is reversible. It is highly probable, however, that the reverse reactions are not always easily effected. Lemberg (18) has shown, for example, that while sodium chloride may almost completely replace calcium from certain silicates, the reverse substitution in certain cases is quite difficult to accomplish, and apparently never becomes complete, though in other silicates calcium and sodium are mutually replaceable.

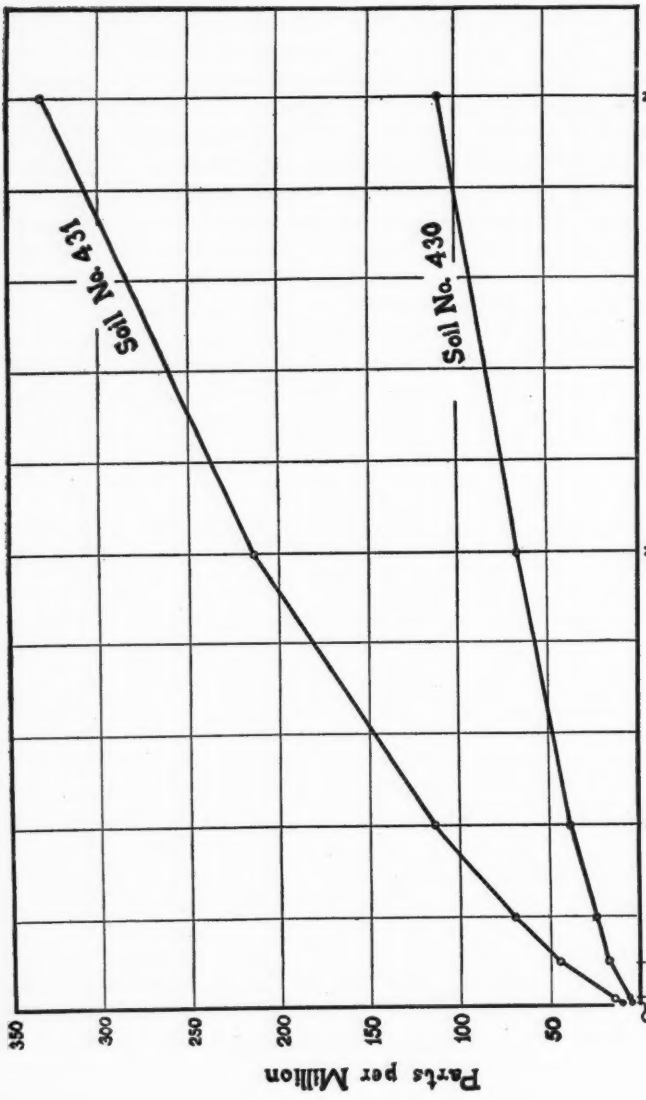

FIG. 7. GRAPHS SHOWING THE EFFECT OF CONCENTRATION OF NaCl ON THE REPLACEMENT OF Ca IN SOILS

It is reasonable to infer, therefore, that treating a soil with a salt solution not only brings about changes in the liquid components of the system represented by the soil, but also alters the chemical nature of some of the components of the solid phase as well. McCool and Millar (21) have shown, for example, that the solubility of soils after leaching in the presence of calcium sulfate is substantially greater than when leached without the addition of this salt. If a soil be subjected to prolonged reaction with sodium or magnesium salts and provision at the same time be made for removing the soluble products of the reactions, such as is afforded by leaching or the growth of crops, the reactions will continue until ultimately a greatly changed chemical system will result. Brief treatment, of course, will produce less pronounced changes; yet we must conclude that only very limited treatment with a soluble salt inevitably leaves its imprint on soils. It is probable that no soil is composed of exactly the same chemical individuals subsequent to treatment with salts, as it did previous to treatment. The physiological significance of these facts will be discussed elsewhere.

SUMMARY

1. Chemically equivalent solutions of the chlorides, sulfates and nitrates of a given base, produced substantially equivalent chemical reactions in the soils studied.

2. The solubility of the anion of the neutral salt solutions was not materially affected by the soils studied, but an exchange of bases took place, with the result that a portion of the base of the added salt passed out of solution and a chemically equivalent amount of other bases was set free from the soil silicates.

3. In the extent to which the simple salts produce these reactions with the soils studied they stand in the following ascending order: calcium, sodium, ammonium, potassium and magnesium.

4. Calcium is the base most readily replaced from these soils, but the solubility of magnesium and potassium also was increased to some extent. It is not certain that significant amounts of sodium were set free by any of the salts used.

5. Considerable amounts of PO_4 were precipitated by each of these soils.

6. Chemical reactions take place between soils and alkaline solutions which result in the conversion of normal carbonate into bicarbonate, a material lowering of the OH-ion concentration of the solution and the precipitation of greater amounts of the cation of the solution than takes place with neutral solutions.

7. The reactions between neutral salts and soils are dependent on the concentration and apparently obey the principle of mass action. Evidence has been obtained that the reactions are reversible.

8. It has been pointed out that the solution remaining in contact with the roots of plants following the addition of a soluble salt to soils must necessarily be different from that of a simple aqueous solution of the added salt. Bases are brought into solution from the soil silicates the amounts of which will vary in different soils, and the OH-ion concentration of alkaline solutions may be very materially lowered. Unless these facts are recognized, totally erroneous conclusions may be drawn concerning the relative toxicity of different salts and the alkali tolerance of different plants.

9. It is suggested that the continued addition of soluble salts in the open field where the products of the reactions are removed by either the growth of crops or intermittent leaching must ultimately result in building up a chemical system different from that originally present. As will be shown later, the physical properties of the system also may be materially altered.

REFERENCES

(1) Bouyoucos, George J. 1917 Classification and measurement of the different forms of water in the soil by means of the dilatometer method. Mich. Agr. Exp. Sta. Tech. Bul. 36.

(2) Bouyoucos, George J., and McCool, M. M. 1916 Further studies on the freezing point lowering of soils. Mich. Agr. Exp. Sta. Tech. Bul. 31.

(3) Burd, John S. 1919 Rate of absorption of soil constituents at successive stages of plant growth. *In* Jour. Agr. Res., v. 18, no. 2, p. 51–72.

(4) Eichhorn, H. 1858 Ueber die Einwirkung verdünnter Salzlösungen auf Silicate. *In* Pogg. Ann. Phy. Chem., Bd. 105, p. 126–133.

(5) Harris, Frank S. 1915 Effect of alkali salts in soils on the germination and growth of crops. *In* Jour. Agr. Res., v. 5, no. 1, p. 1–53.

(6) Harris, F. S., and Pittman, D. W. 1918 Soil factors affecting the toxicity of alkali. *In* Jour. Agr. Res., v. 15, no. 5, p. 287–319.

(7) Headley, F. B. 1920 Unreliable experimental methods of determining the toxicity of alkali salts. *In* Science, n. s., v. 51, no. 1310, p. 140–141.

(8) Henneberg, W., and Stohmann, F. 1859 Ueber das Verhalten der Ackererde gegen Lösungen von Ammoniak und Ammoniaksalzen. *In* Jour. Landw., Bd. 3, p. 25–47.

(9) Hoagland, D. R. 1917 The effect of hydrogen and hydroxyl-ion concentration on the growth of barley seedlings. *In* Soil Sci., v. 3, p. 547–560.

(10) Hoagland, D. R. 1918 The freezing-point method as an index of variations in the soil solution due to season and crop growth. *In* Jour. Agr. Res., v. 12, no. 6, p. 369–395.

(11) Kearney, Thomas H. 1920 The relative absorption by soil of sodium carbonate and sodium chloride. *In* Soil Sci., v. 9, no. 4, p. 267–273.

(12) Kearney, Thomas H., and Cameron, Frank, K. 1902 Some mutual relations between alkali soils and vegetation. U. S. Dept. Agr. Rpt. 71.

(13) Kelley, W. P. 1917 The action of precipitated magnesium carbonate on soils. *In* Jour. Amer. Soc. Agron., v. 9, no. 6, p. 285–297.

(14) Kelley, W. P., and Thomas, E. E. 1920 The effects of alkali on citrus trees. Cal. Agr. Exp. Sta. Bul. 318.

(15) Le Clerc, J. A., and Breazeale, J. F. 1920 Effect of lime upon the sodium-chloride tolerance of wheat seedlings. *In* Jour. Agr. Res., v. 18, no. 7, p. 347–356.

(16) LEMBERG, J. 1870 Ueber einige Umwandlungen findländischer Feldspathe. *In* Ztschr. Deut. Geol. Gesell., Bd. 22, p. 335–372.

(17) LEMBERG, J. 1872 Ueber die Contactbildungen bei Predazzo. *In* Ztschr. Deut. Geol. Gesell., Bd. 24, p. 187–264.

(18) LEMBERG, J. 1876 Ueber Silicatumwandlungen. *In* Ztschr. Deut. Geol. Gesell., Bd. 28, p. 519–621.

(19) LEMBERG, J. 1877 Ueber Gesteinsumbildungen bei Predazzo und am Monzoni. *In* Ztschr. Deut. Geol. Gesell., Bd. 29, p. 457–510.

(20) LIPMAN, C. B., AND GERICKE, W. F. 1918 Does $CaCO_3$ and $CaSO_4$ treatment affect the solubility of the soil constituents? *In* Univ. Cal. Pub. Agr. Sci., v. 3, no. 10, p. 271–282.

(21) MCCOOL, M. M., AND MILLAR, C. E. 1920 Effect of calcium sulphate on the solubility of soils. *In* Jour. Agr. Res., v. 19, no. 2, p. 47–54

(22) PETERS, C. 1860 Ueber die Absorption von Kali durch Ackererde. *In* Landw. Vers. Stat., Bd. 2, p. 113–151.

(23) STEWART, GUY R. 1918 Effect of season and crop growth in modifying the soil extract. *In* Jour. Agr. Res., v. 12, no. 6, p. 311–368.

(24) SULLIVAN, EUGENE C. 1907 The interaction between minerals and water solutions with special reference to geologic phenomena. U. S. Geol. Survey Bul. 312.

(25) VAN BEMMELEN, J. M. 1888 Die Absorptionsverbindungen und das Absorptionsvermögen der Ackererde. *In* Landw. Vers. Stat., Bd. 35, p. 69–136.

(26) WAY, J. THOMAS 1850 On the power of soils to absorb manure. *In* Jour. Roy. Agr. Soc. England, v. 11, p. 313–379.